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A REVISION

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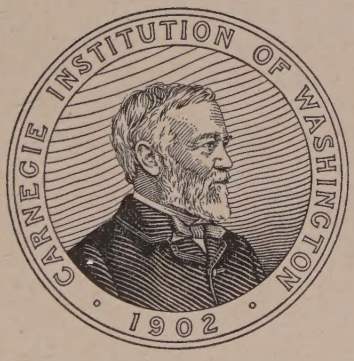
OF THE

Atomic Weights of Sodium and Chlorine

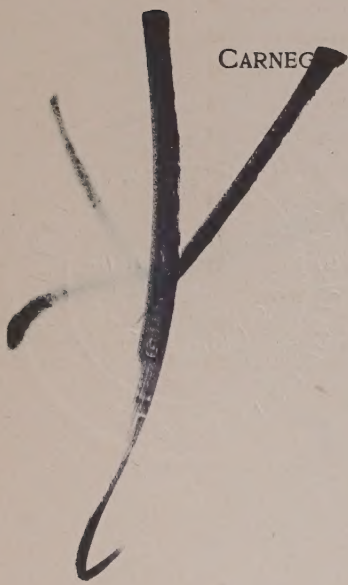
BY

THEODORE WILLIAM RICHARDS, 1868-1928
AND
ROGER CLARK WELLS
OF HARVARD UNIVERSITY



G23318

WASHINGTON, D. C.:
Published by the Carnegie Institution of Washington
April, 1905



CARNEGIE INSTITUTION OF WASHINGTON, PUBLICATION NO. 28.

PRESS OF
HENRY E. WILKENS PRINTING CO.
WASHINGTON, D. C.

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A Revision of the Atomic Weights of Sodium and Chlorine.

By Theodore William Richards and Roger Clark Wells.

INTRODUCTION.

The investigation of the atomic weights of the extremely common elements sodium and chlorine was undertaken because of an unaccountable discrepancy which appeared in the composition of a sample of very pure sodic bromide, as compared with the results of Stas. This sodic bromide had been prepared for the purpose of determining the transition temperature of its hydrated crystals; and a preparation which yielded a constant transition point, therefore giving evidence of great purity, nevertheless possessed a perceptibly lower combining weight than that indicated by Stas's results.

Such a discrepancy as this was not to be passed over lightly. It indicated either an unknown constant impurity in our sodic bromide —and hence a possible error in our transition temperature—or else a flaw in the classical work of Stas. When the first cause of disagreement had been carefully sought in vain, the second was pursued.

Thus a physico-chemical investigation demanding great purity of materials led to a quantitative research of unexpected magnitude; and in turn this quantitative investigation depended continually upon physico-chemical methods and considerations. In confirmation of previous work at Harvard, it was found that the physico-chemical conditions of experiment were of as serious import as the purity of the materials, and of far greater significance than an increase in the scale of operations. The essential circumstances here defined must receive consideration in any other research of a similar kind.

It is needless to say that an investigation seeking to test the accuracy of Stas's work is a serious undertaking, for undoubtedly much of his work deserves a rank among the most accurate of quantitative chemical results; certainly he distanced all those who preceded him.

Nevertheless, he was by no means infallible, as his long oversight of the solubility of argentic chloride, his difficulty in obtaining colorless ammonic bromide, the uncertainty concerning the oxygen in his silver, and the recent proof of an important error in his work on iodine,* all testify. Moreover, Stas's work is not to be considered as accurate in proportion to the scale of his experiments, as many have been inclined to suppose. Mere increase in quantity of material can avail nothing if the same physico-chemical error or the same chemical impurity contaminates the whole. Indeed, it is doubtful if beyond a moderate scale of operations increase of quantity decreases even the probability of accidental error. For example, the extreme variations in his work on the synthesis of argentic chloride, in which on the average nearly 200 grams of the compound were weighed in each analysis, amounted to 0.006 per cent, or 12 milligrams of material.† An accuracy of 0.6 milligram with 10 grams of substance, very easy to attain as far as the collection and weighing of the material is concerned, would have brought him as good agreement. But large quantities have no advantage to offer besides the increased accuracy in weighing and the diminished percentage effect of a given accidental loss of material in transference. For this reason the use of extremely large quantities must rather be considered as evidence of a lack of sound judgment than an index of unusual accuracy. Stas himself acknowledged this by using only about 10 grams of material in each of his last experiments.‡

Regretfully one must admit that a critical study of the work of Stas upon sodium in particular reveals several possibilities of error, as well as at least one inconsistency. He analyzed both the chloride and the bromide; of these salts the former received the greater attention, and will be discussed here in greater detail.

In reviewing his results upon sodic chloride there are two series to be considered, separated by an interval of time of over twenty years. Although at first sight these two series seem to have yielded almost identical results, as a matter of fact they are essentially inconsistent with one another. Both results were obtained by the method of Gay-Lussac, titrating weighed amounts of silver in solution with salt; but at the earlier time the latter was added until all precipitation ceased, while at the later time equivalence was assumed when the supernatant liquid gave equal opalescence with excess of either chloride or silver.

*The work of Ladenburg and Scott has been confirmed by Dr. G. P. Baxter, of Harvard University, whose recent analyses show that the atomic weight of iodine can hardly be lower than 126.97. Proc. Acad., **40**, 419 (1904).

†J. S. Stas, Oeuvres complètes **1**, 341 (Brussels, 1894). ‡Oeuvres, **3**, 503.

Anyone with experience will recognize that a much higher apparent atomic weight of sodium was to be calculated by the first procedure than by the second, other conditions being the same, and yet the results were almost identical. The immediate inference is, of course, that some other condition or conditions must have varied in order to compensate for the effect of the altered method of titration. This inconsistency, which appears also in his work on potassium and ammonium, has never been explained, and one of the functions of the present work was to account for it.

Among the possible sources of error in Stas's work, the most serious seems to have been the practice of dropping solid salt into the solution of argentic nitrate.* Of course this practice caused the greater part of the argentic chloride to be precipitated in the presence of a concentrated solution of salt, immediately around the solid—a circumstance tending greatly to promote the occlusion or inclusion of sodic chloride in the precipitate. Stas, in his early work especially, was fully awake to the danger of the occlusion of *argentic nitrate* in this precipitate; † but he seems to have had no fear of occlusion of other salts. In the sequel we shall show that the chloride of silver tends to carry down with it many salts from their concentrated solution, and that the details of treatment determine whether or not these impurities may be removed by washing.

Another possible cause of the discrepancy is to be found in the methods used for preparing the materials. In Stas's earlier investigation, where the analytical end-point was erroneous, greater care was taken in preparing the sodic chloride than in the later experiments. In general, when purifying this salt, he employed violent treatment, and very rarely recrystallized or in any way fractioned his material afterwards. His favorite method was fusion with ammonic chloride and ammonic chlorplatinate. Presumably the ammonic chloride was used to expel other halogens, and the deposited platinum, Stas believed, carried down silica and alumina with it. Except for these possible advantages, this admixture of foreign materials seems to be a doubtful expedient. In the ten experiments of 1860,‡ six different preparations were made, from the following sources:

1. Sodic carbonate neutralized with hydrochloric acid.
2. Rock salt recrystallized.
3. Sodic sulphate repeatedly fused with ammonic chloride.
4. Sodic tartrate recrystallized and fused with ammonic chloride.
5. Sodic nitrate, similarly treated.
6. Sodic chlorplatinate recrystallized and fused.

*Oeuvres, 1, 759; also 3, 479. †Oeuvres, 1, 337. ‡Oeuvres, 1, 365.

The final step in every case consisted, as usual, in mixing the salt with ammonic chloride and ammonic chlorplatinate, fusing until colorless, and decanting the fused mass from the residue. The ten results agreed almost exactly, indicating that the preparations were, at least, identical; but, of course, the results are all in error, because of the erroneous end-point.

Only two preparations were used in the four experiments of 1881.* For one of these, impure sodic bicarbonate was neutralized with hydrochloric acid. The salt, after three recrystallizations, was repeatedly fused with ammonic chloride and chlorplatinate.† By evaporating a solution of the resulting salt with chlorplatinic acid, it was converted into sodic chlorplatinate without fractionation of any kind. About nine-tenths of this material was dissolved in water. Stas assumed that any potassic salt would not then dissolve; but this possibility is by no means excluded. The first lot of crystals from the solution was decomposed and fused, and the resulting sodic chloride used in the first two experiments. A second and third lot were also obtained from the mother liquor of the first lot. The salt made from the third lot was employed in the fourth experiment of 1881. Thus there were only four crystallizations between the starting point (which was admittedly impure) and the final product; and the first three of these crystallizations were of common salt, isomorphous with potassic chloride. In the third experiment of 1881, the salt was made by neutralizing pure acid sodic carbonate and repeatedly fusing with ammonic chloride in platinum, with no fractionation at all. These specimens were probably less pure than the earlier ones.

Thus it appears that every preparation of Stas was fused in contact with platinum, which was usually in a finely divided "nascent" condition, or at least in the presence of decomposing ammonic chloride. The question is therefore important whether or not platinum can dissolve in melted salt at the temperature of 800°. We have found that fused salt when pure has but a very slight dissolving effect upon platinum, but in the presence of ammonic chloride or hydrochloric acid at a red heat in the presence of air a noticeable quantity of platinum is dissolved, as is indicated by the loss of weight of the containing crucible. It seems likely, then, that Stas's material contained traces of platinum, either in a very finely divided state or possibly as a platinum salt; but the amount could hardly have been large. Stas invariably found non-volatile residues in his preparations, consisting of silicates of sodium and calcium, which he discovered by vaporizing the salt. These residues usually amounted to about 0.004 per cent.

*Oeuvres, 1, 755. †Oeuvres, 1, 685.

It is not impossible, however, that yet other impurities might have volatilized with the sodic chloride. In volatilizing his salts, Stas used a boat of pure platinum.* It is possible that pure platinum would itself have volatilized appreciably at the temperature required to drive off 10 grams of salt in half an hour.† For either of the two reasons just given, Stas's correction for impurity in his salt would not have been large enough.

These impurities must, however, have been almost equally present in the early and later samples, and could not explain the serious discrepancy between them. At most, however, as we shall show, they could hardly have exceeded 0.01 per cent, an amount much smaller than the discrepancy in question. Our own experience shows that common salt is a substance very easy to prepare in a pure state. Clearly the cause of the discrepancy must be sought elsewhere.

The other essential substance, to be prepared in a pure state, was silver. This Stas prepared in a variety of ways, as is well known; but for all this work the silver was either cast in ingots from under an oxidizing flux, or else "granulated" by dropping into water. His criterion of pure silver was the melting of the surface of a button without any apparent irregular expansion as it liquefied, or any flame-color, and the absence of all specks and spots from the completely melted globule. In all experiments it was reddened in a silver crucible before weighing.

After Dumas had recommended the fusion of silver in a vacuum, Stas made many experiments upon the occlusion of gases by silver. He carefully investigated the samples of silver used in his atomic weight researches, and also new preparations. He found that fusion in a flux of sodic nitrate introduced a quantity of oxygen, and that bars and blocks were slightly purer than "granulated" silver. In no case was the amount of retained gas found by Stas enough to affect seriously even a very accurate analysis; but, as will be shown later, it is probable that he did not find all the oxygen present. An error in Stas's silver would not account for the discrepancy between his results on sodium and ours; for an impurity in the silver would cause his atomic weight of sodium to appear too low, and not too high. On the other hand, the impurity in Stas's silver is undoubtedly the cause of the difference between his atomic weight of chlorine and ours.

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*Oeuvres, 1, 681.

†See Hall, J. Am. Chem. Soc., 22, 494 (1900); Richards and Archibald, Proc. Am. Acad., 38, 460 (1903); Hulet and Berger, J. Am. Chem. Soc., 26, 1512 (1904). There seems to be no doubt that platinum is slightly volatile at 1,000° in the presence of air. Probably it is not in pure nitrogen.

From these considerations it was clear that the reason for the incompatibility of the results on sodium was probably to be sought chiefly in the method of analysis rather than in the impurity of the materials. The long-continued search for the causes of discrepancy led finally to a satisfactory explanation of the whole anomaly. In order to make this clear, the details of our own investigation must be recounted.

BALANCE AND WEIGHING.

The Troemner balance which has served in many similar researches was used during most of the present work.* Successive weighings on it of the same object rarely differed as much as 0.03 milligram. For a few of the conclusive final experiments a yet more sensitive and perfect balance, especially made for this kind of work by the same maker, was used.

The Sartorius weights were standardized from time to time by the method devised by one of us.† It was found as usual that the larger gold-plated and platinum-plated brass weights very slightly changed from time to time, although the smaller platinum weights did not. All weighings were made by substitution. Furthermore, the major portion of the substituted tare consisted of a counterpoise exactly similar to the crucible, tube, or boat which was being weighed. Thus the weights required were never large in amount and errors due to changes in meteorological conditions were avoided. The method of recording and checking the weights is given in another place.‡

While these obvious particulars are given here for the sake of completeness, it must be remembered that accuracy of weighing is easily attained. The great errors in chemical quantitative work are usually not in the weighing, but are due rather to impurities in the substances weighed or incompleteness or irregularity of reaction. Only in a few cases, with large vessels, was it necessary to use a telescope for reading the vibrations, the observer being in another room and looking through an intervening glass door.

The balance-room devoted to these most accurate determinations was kept at a very constant temperature, being wholly inside a private laboratory whose air temperature was regulated by a delicate thermostatic attachment to its heating apparatus. The balance-room itself had neither heating apparatus nor outside windows. This question of constancy of temperature is of the most vital importance in the weighing of large vessels.

*Proc. Am. Acad., **26**, 242 (1891).

†Richards, J. Am. Chem. Soc., **22**, 144 (1900).

‡Richards, Proc. Am. Acad., **31**, 175 (1895); Z. Anorg. Chem., **10**, 19 (1895).

In reducing weights in air to weights in vacuum, the densities at about 20° were assumed to be as given below. The value for silver proceeds from Stas, and was checked by one determination by us of the purest silver (sample W, described later). The value for the brass weights refers to the gold-plated Sartorius weights used in all but a very few of the experiments; the other set had a slightly higher density, of which account was taken. The correction for 1.000 gram of substance weighed in dry air at 20° and 760 mm. is stated for each substance.

Substance.	Density at 20°.	Correction for one gram of substance, 20°, 760 mm.
Silver.....	10 49	— 0.000029
Sodic chloride....	2.14	+ .000418
Silver chloride....	5.56*	+ .000073
Weights.....	8.40	.....

Especially when sodic chloride or silver chloride was weighed the temperature and barometric pressure were recorded at the time of weighing. In case of significant variations of temperature or pressure the corrections were changed accordingly. The correction is computed as follows:

Correction $= w$ (volume of 1 gram of substance — volume 1 gram of weights), where w is the weight of 1 cubic centimeter of air at the given temperature and pressure. The following small table contains a sufficiently accurate statement of this value in convenient form for use with a logarithmic slide rule.

Value of w, in grams.

Temperature (°C).	750 mm.	760 mm.	670 mm.
14°.....	0.001214	0.001230	0.001246
16°.....	.001205	.001221	.001237
18°.....	.001197	.001113	.001229
20°.....	.001189	.001204	.001220
22°.....	.001181	.001196	.001212
24°.....	.001173	.001188	.001204

If the air is completely saturated with water vapor the above values should be decreased by 0.000008 at 14°, 0.000010 at 20°, and 0.000013 at 24°. But since the air of our balance cases was certainly less than a quarter saturated with moisture, any correction on this account would have been supererogatory.

*Richards and Stull, in an investigation as yet unpublished.

PREPARATION OF PURE MATERIALS.

WATER.

The traces of organic impurity in the distilled water of the laboratory were eliminated by redistilling from a weakly alkaline solution of potassic permanganate, using at first a glass condenser and rejecting the first quarter of the distillate. Water thus prepared was pure enough for preliminary nephelometric work, when the presence of a trace of alkali could do no harm; it was usually kept in Jena flasks. In cases where the greatest purity was desired it was distilled, of course, once further, and for the nephelometric experiments it was kept in a closed bottle provided with a siphon and protected from possible traces of hydrochloric acid by a tube containing sodic hydroxide. For final preparations and accurate analyses, where silica and alkali must be excluded, the water was condensed and collected during the third distillation wholly in platinum. Care was taken to exclude dust in all stages of the proceedings; for, although visible dust might weigh little, its presence in silver halogen salt would produce decomposition and loss of weight in the final fusion. Only one who has attempted to exclude all dust from solutions can appreciate the difficulty of doing so. Thorpe and Rodger,* working upon viscosities, found that sealed-in condensers were very helpful in excluding dust from their distillates. We did not go as far as this, but the danger was borne in mind at every stage of the work and guarded against.

HYDROCHLORIC ACID.

For the final work the purest acid of commerce was treated with a few crystals of potassic permanganate, diluted, and boiled. This should have expelled bromine and iodine, and must have oxidized any trace of organic matter which might have been present. The oxidation and boiling were repeated; the solution was fractionally distilled; and for the succeeding treatment the middle fraction was selected and subjected to another distillation, in which a platinum condenser and receiver were employed. As a matter of fact, most of these precautions were found to be unnecessary, since salt made, as described on page 16, from the best "chemically" pure acid of commerce only once redistilled in platinum, without any further precautions, gave the same results as the purest material.

*Phil. Trans., 185 A, 432 (1894).

SODIC CHLORIDE.

In most cases a perfectly pure salt can not be made by precipitating the impurities, as many are prone to assume, but must itself be precipitated or crystallized from the less pure solution. Sodic chloride is nearly insoluble in a concentrated solution of hydrochloric acid; therefore the usual method of precipitation by means of hydrochloric gas seemed the best possible method of obtaining pure sodic chloride, since any included hydrochloric acid could be completely expelled by fusion. This expectation was confirmed by trial, and when it had been found that this means of purification was unusually suitable, most of the specimens of salt were treated in this way. This and other purifications were greatly assisted by centrifugal draining of the crystals. For this purpose salt was collected in a platinum funnel, and this was covered and supported on a stout frame capable of being whirled by means of strong cord about a radius of a meter. A test-tube, firmly fixed in the frame, collected the separated mother liquor. Centrifugal draining, so important in technical work, has hardly received the attention which it deserves in the scientific laboratory. Experiments have shown that a good centrifugal apparatus is capable of separating nine-tenths or more, according to the habit of the crystals, of the mother liquor which would otherwise contaminate the solid, hence making the purification at least ten times as effective as it would otherwise be.* The whole treatment of precipitation and draining was carried on in platinum vessels which had been effectively freed from superficial iron.

Besides this chief mode of purification, others were used in special cases, and the original material came from a variety of sources, as recorded below. One of these was Merck's purest sodic chloride, which this firm stated had been prepared from German rock salt. Another was the very pure sodic sulphate prepared for the experiments on the transition temperature of this substance, and known to be very pure, because of the constancy and accuracy of its transition point (32.383°).† Another was a fine specimen of Stassfurt halite, perfectly clear and colorless. A fourth specimen was made from the purest sodic bicarbonate manufactured by the Solvay Process Company, of Syracuse, New York, and very kindly furnished in large quantity by that company. A fifth sample was made from pure sodic carbonate from Merck. These preparations, differing widely in the steps of manufacture, and in geographical source, all yielded essentially the same atomic weight.

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*Richards, Journ. Am. Chem. Soc., **27**, 104 (1905).

†Richards and Wells, Proc. Am. Acad., **38**, 431 (1902); also Zeitschr. phys. Chem., **43**, 465 (1903).

The source of the materials having been given above, it remains to record the details of their preparation.

In the first place, a large quantity of Merck's sodic chloride, which had been purified from German rock salt, was thrice reprecipitated by hydrochloric acid. This salt is designated "sample A" below, and was used in preliminary experiments. It was further crystallized from water (B); some of this was fused with ammonic chloride and ammonic chlorplatinate (C); a portion was then precipitated with hydrochloric acid (D); and finally some was again fractionated from water (E). None of these operations seemed to have any essential effect upon the combining weight of the salt; hence, even Sample A must have been practically pure.

The very pure sodic sulphate was easily converted into chloride by successive precipitation from solution by means of gaseous hydrochloric acid. The sulphate forms an especially fortunate source of pure sodium, since none of the other alkaline sulphates yield crystals of the same degree of hydration or the same crystal form. Hence sodic sulphate which has been many times recrystallized must be extremely pure. The ease with which a constant transition temperature may be obtained is evidence of this.

A specimen of sodic sulphate, which had been shown to be pure by its transition temperature, was twice further recrystallized before adding hydrochloric acid. Four precipitations by this gas, with washings and drainings, removed practically all of the sulphuric acid. Nevertheless, when the mother liquor was concentrated by evaporation and tested, an extremely small trace of sulphate was found by excess of baric salt to persist until the tenth precipitation. There was no trace of visible baric sulphate on testing the mother liquor, even in the nephelometer, after the eleventh precipitation, but the salt was precipitated once more for certainty. This salt, thus twelve times separated by hydrochloric acid, was designated F. It seems highly probable that since so large an amount of sulphuric acid was eliminated from it by this treatment, all other impurities must have been separated.

For another specimen of salt, a number of fine, large, colorless transparent crystals of halite, from near Stassfurt, Germany, were dissolved in pure water. After the addition of a little sodic hydroxide, boiling, and standing, the solution was filtered and precipitated with hydrochloric gas. A solution of the latter salt in water stood several days. The clear decanted portion was precipitated twice more, fractionally crystallized from water, and dried over sodic hydroxide in a vacuum desiccator. This specimen was called sample G.

The bicarbonate from Syracuse, New York, was of the following composition, according to the report of the Solvay Process Company:

	Per cent.
Silica	0.006
Ferric oxide and alumina	.002
Calcic carbonate	.030
Magnesic carbonate	.005
Sodic chloride	.070
Sodic carbonate	.522
Sodic bicarbonate	99.300

This material, already very pure for a commercial substance, was easily further purified by repeated washing with cold water, which was sufficient to remove most of the chloride.

A portion of the Syracuse bicarbonate, thus washed four times with cold water and thoroughly drained each time with a reverse platinum filter, was nearly all dissolved in water. After settling, the resulting clear solution was decanted, neutralized with hydrochloric acid, and then evaporated to dryness. The sodic chloride was fused in platinum, dissolved, and considerably diluted. After long standing the clear upper portion was decanted from very finely divided silica. This method of fusion is a very effective means of separating silica, but the precipitate is so fine as to require a long time to settle, and as to run through most filtering septa. Hence cautious decanting, with rejection of the considerable lower portion of the solution, is necessary. The unimpeachable solution of salt thus obtained was concentrated and twice precipitated by hydrochloric gas (H), twice more precipitated (I), and yet twice more precipitated (J). Analysis showed these three to be alike, as will be recorded.

The Merck bicarbonate was thoroughly washed and once recrystallized from water. It was then gently ignited, and the normal carbonate was three times crystallized from water. From this carbonate, by the usual process of precipitation by hydrochloric gas and crystallization from water, sample K was prepared. This sample gave essentially the same combining number as the others.

With such conclusive evidence that no foreign base was present, we turned our attention to the acid. The preceding preparations had all been precipitated with hydrochloric acid gas, obtained simply by warming the highly concentrated purest acid of commerce, because we deemed it more convenient to use this constant material, even if slightly impure, than to prepare so large a quantity of the purest acid. A special set of comparative experiments, made with the purest acid, proved that the other material had, as a matter of fact, been pure enough for the most exacting requirements.

For this purpose the very pure hydrochloric acid was used whose preparation is described above (p. 12). This acid was neutralized by an especially prepared sample of soda, made from a second portion of the Syracuse bicarbonate. The purification was conducted wholly in platinum vessels, of course. After being washed as before, the bicarbonate was dried and heated, to convert it into the normal carbonate. The solution of the latter in water was decanted daily as long as any precipitated residue (calcic carbonate) appeared visible. The sodic carbonate was then recrystallized four times, as the deka- or hepta-hydrate, and once as the anhydrous salt. A concentrated solution of the latter salt was then treated for a considerable time with carbon dioxide under a bell jar until the bicarbonate had formed. The carbon dioxide was made by gently heating sodic bicarbonate, and was well washed with pure water. The pure bicarbonate thus formed was washed with cold water, thoroughly drained, and dissolved in an excess of the pure hydrochloric acid. The resulting salt was twice fractionally recrystallized from water on the steam bath; and the crystals were washed and drained each time, in order to free them from any possible calcium or magnesium chlorides, which are not easily eliminated from carbonate. Since the atomic weight from this preparation (L) was identical with that from the preceding preparations, the previous salts, made by precipitation with hydrochloric gas, could have contained no other halogen than chlorine.

It appears from the identity of all these specimens that sodic chloride is among the substances whose preparation in a pure state is an easy problem. It is further true that the expulsion of water from it upon fusion without loss of halogen is a very simple matter; moreover, since we succeeded in proving that salt fused in a vacuum possesses the same combining weight as that fused in air, the solid contains neither occluded oxygen nor nitrogen in weighable amounts. This matter is discussed further on page 55.

Considering these experiments, it is fairly safe to infer that all the various preparations of sodic chloride were quite free from significant quantities of any foreign substance.

SILVER.

Recrystallized silver nitrate served as the starting point for the first specimens, and the already purified residues from the early experiments were again converted into pure silver for later use. Many samples were prepared from different sources.

The silver used in all the experiments on sodic chloride was at first purified by precipitation as chloride and then recovered by reduc-

tion of the chloride with invert sugar* and sodic hydroxide. While it is true that this process is not the best for the final treatment of the silver, the precipitation as chloride is an excellent step in the preliminary purification. The invert sugar was made from a filtered solution of "rock sugar." No metals were found in it by electrolytic treatment. The sodic hydroxide used, after settling and decantation, had been electrolyzed until iron was completely removed. This slow but effective way of removing foreign metals was hastened by using a rotating cathode, while a fixed anode stirred the solution. The argentic chloride was precipitated from a somewhat dilute solution, to avoid the occlusion of impurities, and must be thoroughly washed. It is best to wash at first with cold water, in order to avoid the contraction of the precipitate. The reduction was carried out in a silver dish to avoid the introduction of silicates. This precaution is not needed when electrolytic purification is to follow. In some cases, where the original material was not wholly free from suspicion, the precipitation as chloride and reduction were repeated. After reduction, the washed silver was fused upon either sugar charcoal or pure lime, before the blast lamp, whose nozzle was scrupulously cleaned. If the large buttons of metal thus formed are not kept hot too long and are cooled in a reducing flame, they are already extremely pure.† For ordinary work, or even for work on atomic weights of usual accuracy, its purity suffices. Nevertheless, it can not be considered as perfectly pure, for it must contain, perhaps, 0.001 per cent of sulphur and variable traces of carbon from the illuminating gas (or else oxygen from the air), as well as an occasional trace of argentic chloride, arising from incomplete reduction. When thus cooled it is likely to contain numerous minute cells inclosing gas.

As one stage in the purification the electrolytic method used by J. L. Hoskyns Abrahall has many advantages.‡ The almost pure material just described is made the anode of a cell containing a concentrated solution of argentic nitrate prepared from the same silver. The cathode is a pure silver wire, upon which is deposited by a properly regulated current beautiful crystals of electrolytic silver. The finely crystalline powder which falls from the anode§ may be easily

*According to Stas, saccharose at 100° would have answered as well as invert sugar at 60°. The saccharose is, of course, inverted by the strong hot alkali. Oeuvres, **3**, 13.

†Richards, Proc. Am. Acad., **29**, 65 (1893; Z. Anorg. Chem., **6**, 98 (1893). See also Proc. Am. Acad., **38**, 450 (1903). This work was confirmed in the latter part of the present investigation.

‡J. Ch. Soc. Trans., **61**, 660 (1892).

§Richards and Heimrod, Proc. Am. Acad., **37**, 415 (1902).

collected separately by placing the anode button in a watch glass or low dish, wholly submerged in the electrolyte. In order to exclude every chance of contamination, no metal but silver may be allowed to come in contact with the electrolyte, although the danger from an immersed platinum wire, either at cathode or anode, is obviously slight. Three samples of silver were thus prepared, called respectively M, N, and P. This silver must have been free from every conceivable impurity, except about 0.02 to 0.05 per cent of the mother liquor from which it was deposited.* This important impurity, consisting wholly of water and argentic nitrate, can be eliminated only by fusing the silver, a matter which will soon be discussed.

Besides this very pure material used in the work on sodium, several new samples of at least equal purity were made for the even more critical work on chlorine. Three of these new preparations were made from thrice crystallized pure argentic nitrate. A portion of this nitrate was converted into argentic chloride and reduced by pure invert sugar and purified sodic hydroxide. A second portion was reduced by the invert sugar and sodic hydroxide. A third portion was reduced by ammonic formiate and ammonic acetate as recommended by Stas.† Some of each of these lots was deposited by electrolysis in a concentrated silver nitrate bath in the usual way (S, T, U, respectively).

Not content with these preparations—although all appeared to be equally pure—and anxious to leave no stone unturned whose lifting might disclose some new source of error, we made yet two more preparations with new precautions. For one of these, through the great kindness of Mr. Richard Pearce, of the Boston and Colorado Smelting Works at Argo, Colorado, a specimen of metal was secured whose source and history were known as far back as possible. Below is given Mr. Pearce's statement concerning it:

> This specimen is the product of the treatment of ores mainly from Colorado, in which it occurs associated with quartz, barite, calcite, pyrite, sphalerite, with more or less copper in the form of chalcopyrite, together with small quantities of arsenic, antimony, lead, bismuth, and tellurium. The silver minerals are chiefly argentite, polybasite, pyrargyrite, proustite, tetrahedrite, stephanite, and occasionally cerargyrite. A small percentage of the silver comes in copper mattes purchased in other districts, more particularly Montana, where the silver ores are much the same in character, and are smelted with copper ores, forming a matte containing about 200 ounces of silver per ton.
>
> The roasted ore is mixed with others, principally siliceous, and the mixture is so arranged that, when smelted, it shall yield a slag containing as near as

*Richards and Heimrod, Proc. Am. Acad., **37**, 415 (1902); Richards, Proc. Am. Philos. Soc., **42**, 28 (1903); Zeitsch. phys. Chem., **46**, 189 (1903).

† Stas, Oeuvres, **3**, 40.

possible 40 per cent of silica and a first matte or fusible sulphide which assays 40 per cent of copper, 400 ounces of silver, and 6 ounces of gold per ton.

The first matte always contains a certain amount of lead, but the quantity rarely exceeds 10 per cent. The next stage in the process includes the roasting and concentration of the ore-metal, or first matte, to "white metal" containing 60 per cent of copper.

This white metal is now ready for the extraction of the silver, which comprises the following operations: Rough roasting; fine grinding; fine roasting for sulphate of silver by Ziervogel's process; leaching, and the precipitation of the silver on plates of copper.

In the precipitation of the silver a certain amount of copper is found mixed with the silver in the form of cuprous oxide and of small scales and scraps of metallic copper, and a process of refining is necessary previous to melting. This copper is removed by prolonged boiling with water containing a small quantity of sulphuric acid, into which air is injected by means of a small jet of steam. Sulphate of copper is formed, which is carefully washed out of the silver. The silver is then dried and melted into bars of an average fineness of 99.9 per cent.

The silver came to us in the granulated form obtained by dropping into water, and having been prepared with unusual care, was found to be even purer than Mr. Pearce claimed. After solution in nitric acid, it was crystallized fifteen times from acid solutions with centrifugal draining. The solubility in cold nitric acid is so slight that this train of purification could be effected without serious loss. Even after the second crystallization the salt was free from any observable trace of copper, and all other metallic impurities must have been eliminated before the last crystals were obtained. The pure argentic nitrate was dissolved in pure water and precipitated by hot ammonic formiate, prepared from pure freshly distilled formic acid and ammonia which had been collected in platinum. It is better to use pure ammonic formiate instead of a mixture of ammonic formiate and acetate as Stas did, because in the former case less carbon is included in the cells of the crystals, and, moreover, that which it included occurs in a less dangerous form. Since the reaction takes place according to the equation

$$2AgNO_3 + 2HCOONH_4 = Ag_2 + 2NH_4NO_3 + CO_2 + HCOOH$$

every 170 grams of argentic nitrate need 46 grams of pure formic acid (or about 42 cubic centimeters of 90 per cent acid, with specific gravity 1.2) converted into ammonic formiate. It is necessary to take this double amount in order that the ionized hydrogen (nitric acid) may be removed by the salt of the weaker acid. The precipitation was conducted in good glass. The beautiful white precipitate was washed with the purest water, until the washings gave no Nessler test. This silver, V,* although it had not been electrolyzed, was as pure as any

*The preparation work and analyses of this silver were conducted wholly by T. W. Richards.

which we made, judging from the analysis. The method of purification just described is the most convenient and safest of all. The only improvement which might be suggested is the use of a silver dish for conducting the final precipitation. This improvement was tried in the next preparation.

Part of the silver, not electrolyzed, proceeding from the earlier reduction with ammonic formiate and ammonic acetate (p. 18) was dissolved in redistilled nitric acid. The silver nitrate, once more crystallized, was dissolved in pure water in a large silver dish. Ammonic formiate was freshly prepared by passing pure ammonia gas into redistilled formic acid. With it the silver nitrate was reduced in a silver dish, but otherwise as described above, washed free from ammonia and dried in the same silver dish. This sample was called W.

There is no reason to believe that any of these samples of silver contained any appreciable impurity, except the traces of included mother liquor already alluded to. It is probable that Stas's silver also was equally pure at this stage in the proceedings. The subsequent treatment of the silver, in the effort to eliminate the mother liquor and prepare the metal for weighing, seemed to be in our experiments the only cause of difference in the quantitative behavior of our samples, and there is every reason to believe that Stas introduced during this treatment the impurities which have rendered a revision of his work imperative.

Because of this importance of the subsequent treatment, it is necessary to record a very detailed statement of the precise operations of the present research in this particular, and to point out the differences between these operations and the methods of Stas.

Everyone must agree that fusion alone is the only safe method of eliminating wholly the liquid included in the cells of the crystals, whether these crystals be produced by electrolytic or chemical reduction. The difficulty is to find an environment for the silver during its fusion from which it will not absorb or retain foreign substances.

The question presents a two-fold difficulty, because both the solid support of the silver and the atmosphere which surrounds it must be considered. The former of these difficulties may be discussed first.

In what vessel may the silver be fused, in order to avoid contamination? Stas, in his posthumous work, recommends fusion in a cupel of basic calcic phosphate, in the flame of a blast lamp, and subsequent ignition in hydrogen. This process, while possibly as good as he contends, may nevertheless be a dangerous one. Everyone knows the risk to a platinum crucible of igniting in it a phosphate with reducing material, and yet Stas took no steps to prove the absence

of traces of argentic phosphide from the metal prepared in this way. His own observation, indeed, confirms this suspicion, for he states that silver thus fused in an oxidizing flame became covered with a yellow crystalline film, which instantly disappeared in a reducing flame. The great instability of the oxide of silver affords reason for doubting his assumption that this film was an oxide; it seems more probable that it was a phosphate, produced by oxidation of silver phosphide, and decomposed by reduction to this compound again. Stas, relying entirely upon the superficial appearance of the silver and its flame test as a guide to its purity, would not have discovered the presence of phosphide.

The possibility of this danger is enough to incline the careful chemist to avoid the presence of phosphorus. As a matter of fact, Stas never used silver prepared in this way for his atomic weight researches,* and no one else seems to have used this procedure except Scott,† who fused 5 grams of silver in this way for a single analysis. Of course, however, a single analysis is too slender a basis upon which to form any adequate judgment concerning its purity. Actuated by the preceding considerations, we did not take the trouble to test the method, preferring first to test others which gave more promise of satisfactory results.

Another possible material, which has been partially tested in previous work, is carbon. Sugar-charcoal may be prepared in a state very free from metallic impurities, and would serve excellently if it were not that carbon is probably soluble to a slight extent in the molten metal. We gave this possibility a fair test, and found that when the silver is fused on a cupel of sugar-charcoal with a clean blast lamp and moderately pure illuminating gas, it is as a matter of fact very pure. (Experiments 67, 68, 71, on page 61.) Probably the oxidizing flame used to melt the metal prevents the introduction of much carbon at first, and during the brief reducing period in which the metal must be cooled to eliminate an excess of oxygen there is not time to dissolve much carbon. Evidently, however, a process which depends upon the mutual elimination of opposing errors is an uncertain one, and hence not suitable for the most accurate work. That carbon is really dissolved was well shown by another experiment, in which a carbon boat in a porcelain tube filled with pure hydrogen was used to contain the fusing silver. The experiment yielded silver slightly less pure than the previous average; it must have contained

*Stas, Ouvres Compl., **3**, 75.

†A. Scott, J. Chem. Soc. Trans., **79**, 147 (1901).

0.005 per cent of dissolved carbon. (Experiment 79, p. 61.) Of course, however, a single experiment has but little exact weight in such a case, except to show that the process is probably undesirable.

Returning from these unsatisfactory methods to the one used very early in his career by Stas, we tested once more the use of lime as a support for the fusing silver. This seemed to be an especially appropriate substance for the containing vessel, because it is so easily obtained pure, and because it is so hard to reduce that no metallic calcium could be dissolved by silver. But, of course, the silver must be saturated with dissolved lime, and it remained to be proved that a saturated solution of lime in fused silver is so dilute as to introduce only a wholly insignificant amount of impurity. This was easily shown by actual experiment. Ten grams of silver fused on lime were dissolved in pure dilute nitric acid in a platinum dish and precipitated as sulphide by pure hydrogen sulphide gas, led in through a platinum tube. After filtration on a platinum funnel, the remaining liquid was evaporated to dryness in platinum. The minute trace of residue, probably due to traces of dust, on moistening with hydrochloric acid gave no trace of the calcium bands in a spectrometer which showed them plainly from a solution containing 0.01 milligram of lime in 1 cubic centimeter. Hence it is evident that less than this amount of lime was dissolved by the silver, *i. e.*, less than 0.0001 per cent, if any.

This experiment settled the question concerning the supporting substance, but of course the lime must be perfectly pure. If the lime is partially made from the nitrate, it must be very thoroughly ignited before it is used, otherwise the silver may dissolve some of the oxygen caused by the decomposition of the salt. This was shown by the careful testing of a quantity of silver fused on a new boat, which had not been thoroughly ignited. (Exps. 72 to 76, p. 61.) A boat in which pure silver has already been fused has an advantage in this respect, as well as because every accessible trace of reducible material must have been dissolved out of it. Of course the lime used in the present experiments was especially purified, as will be related.

It is true that even when carefully prepared a boat of lime is likely to be so friable as occasionally to cause a partial coating of the button of silver with the powdered lime, but the great surface tension of molten silver keeps this all on the surface, whence it is easily dissolved by means of the dilute nitric acid always used by us to clean the metal. Scott, who has objected to the use of lime, again on the basis of a single experiment, does not mention having taken this necessary precaution.

All the silver used in the three final series of experiments which follow was thus ignited in pure, well-seasoned lime boats, capable of holding from 30 to 50 grams at each fusion. The unglazed porcelain boats in which the lime was molded were made on purpose for this object by the Royal Berlin Porcelain Manufactory.

The environing atmosphere around the silver during fusion next claims attention, since that, too, may vitiate molten metal. Obviously air is impossible. A vacuum seemed *a priori* to be the best means of preventing the access of impurity, but, to our surprise, we found that silver fused in a vacuum was sometimes less pure than that fused in the open flame of the blast lamp. (Exps. 72 to 76, p. 61.) This puzzling circumstance was ascribed finally to the supersaturation of silver with oxygen, derived either from included argentic nitrate or from the calcic nitrate in the boat.* Silver precipitated by formiate ignited on a pure boat does not show this impurity, because free from oxidizing substances; and a few minutes' ignition in pure hydrogen quickly removes in chemical fashion this supersaturation when it exists, thus purifying the silver. The amount of hydrogen which remains must be on the limit of the weighable; at least, we were unable to detect it quantitatively, because silver fused in hydrogen yielded exactly the same amount of argentic chloride as that containing no oxygen which had been fused in a vacuum. This is shown by the comparison of Exps. 77, 78, 80, 81, 83, and R. 2, with 84, 85, and R. 3 (p. 65). Hence Stas's conclusion that silver does not dissolve over 0.0004 per cent of hydrogen is supported, although indeed his method of preparing the silver was somewhat different from ours, and his method of distinguishing the hydrogen was somewhat doubtful.

The discovery of the residual trace of oxygen in the fused electrolytic metal, which had contained occluded nitrate, was not made until the work on sodium was finished, but fortunately three pieces of the silver used in that work still remained, so that it could be compared with the purest silver which we were able to make. The comparison was made by weighing the chloride obtainable from known weights of each sample, and the details will be recorded in full in the chapter concerning the synthesis of this salt. For the present it is enough to say that the silver used in the work on sodium yielded 0.004 per cent less chloride than the purest silver,† and therefore was

*A trace of chlorine, which, however, could hardly have been present, would have the same effect.

†The average of analyses 65, 66, 70 was compared with the average of the final series (see pp. 61 and 65).

assumed to contain that percentage of impurity. A change of only 0.002 in the atomic weight of sodium was caused by this difference.

All the silver used in the final series of syntheses of silver chloride was free from dissolved oxygen, and three of the specimens must have been free from hydrogen also. The method of treating each is sufficiently specified in the table of results and need not be further discussed here. The silver used in this part of the work was the purest we were able to prepare, and we know of no impurities which it could have contained, except in some cases the insignificant trace of hydrogen already mentioned.

The boat used for the fusion was made from a mixture of pure lime and calcic nitrate, and was contained in a porcelain tube closed with Hempel stoppers. The tube was heated to bright redness in a Fletcher furnace.* The resulting bars of silver were freed from the adhering lime by scrubbing with clean, hard sand and successive treatments with dilute nitric acid. The argentic nitrate was dissolved away by ammonia, and many washings with water were followed by drying the bar in a hard glass tube at about 400° in a vacuum.† Water might otherwise become sealed into the microscopic cavities, often present in fused silver, during the next operation of cutting into blocks. The cutting is best carried out upon a silver plaque by means of a clean steel coldchisel. The blocks thus cut were superficially etched once more with nitric acid, so dilute that a possible trace of iron could not assume the passive state, and the cleaning and drying operations were repeated. The pieces then preserved in a desiccator over potash are ready for weighing and analysis.

After the details of the analysis have been discussed, the relation of the purity of this silver to that of Stas will be made clear.

LIME.

The preparation of pure lime upon which to fuse the silver was a matter of great importance, because of the danger that any impurity in it might contaminate the silver. Its preparation was begun by dissolving marble in nitric acid, boiling with an excess of calcic hydroxide, filtering, neutralizing, and twice recrystallizing the calcic nitrate.‡ Calcic carbonate was then precipitated with ammonic carbonate, repeatedly washed, and finally dissolved in redistilled nitric acid.

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*Proc. Amer. Acad., **30**, 379 (1895).

†The silver used in Experiments R 1, R 2, and R 3 (p. 65) was wrapped in pure silver foil during this ignition to prevent contact with hot glass.

‡Calcic nitrate should be recrystallized below its transition temperature, 44°, a proceeding much facilitated by inoculation with the respective hydrate.

The resulting nitrate, made alkaline with ammonia, was electrolyzed to remove a suspected trace of iron and filtered through a layer of calcic carbonate upon a Gooch crucible. It was found that ammonic carbonate, of variable composition, could be conveniently distilled with steam from its solution. With such a distillate, prepared wholly in platinum, calcic carbonate was again precipitated and well washed. A small portion of this was converted into nitrate.

Ignition of the calcic carbonate to oxide was carried out in porcelain, since platinum is slightly volatile at high temperatures, and might have contaminated the lime. A dry mixture of calcic oxide, with about a fifth its weight of powdered anhydrous nitrate, was packed into specially made large unglazed boats of Berlin porcelain. The molded mixture when heated to redness sintered firmly together and made a chemically pure receptacle, large enough to contain about 50 grams of silver at a time. In order to prevent adhesion of the boat to the glaze of the porcelain tube, the boat should not fit the tube very closely, and it is well to cover the glaze under the boat with a layer of pure powdered lime.

UTENSILS.

Of course all the containing pieces of apparatus—dishes, funnels, crucibles, retorts, condensers, and so forth—were of platinum wherever silica was to be feared and platinum was not itself harmful. In this latter case, according to circumstances, either silver vessels or vessels of the best insoluble glass (Jena, or "nonsol") or porcelain, or in some cases fused quartz, were used. In this way the greatest possible purity of the preparations was assured.

THE SOLUBILITY OF ARGENTIC CHLORIDE.

Mulder pointed out in 1857* that the solubility of argentic chloride is sufficient to affect all quantitative results into which the precipitation of this substance enters. Stas overlooked this solubility in his early determinations, and hence in 1876 repeated some of them.† Other more recent experimenters‡ have in general confirmed Stas's later conclusions about this solubility, so that it is not important here to give a lengthy statement of our further confirmatory results.

There can be no doubt that freshly precipitated argentic chloride is soluble in cold water to the extent of several milligrams per liter, and

*Mulder, Die Silber-Probirmethode. Leipzig, 1859.

†Stas, Ouvres, **1**, 751.

‡For references see Böttger, Zeitsch. phys. Chem., **46**, 189 (1903); Richards, Proc. Am. Acad., **29**, 69 (1893).

that this solubility steadily diminishes, without a very sharp change at any time, as the precipitate remains in contact with the liquid.

A variable solubility of this nature may be due to one of two causes. Either the precipitate is capable of assuming two or more allotropic forms, of which the least stable appears at first,* or else it separates in a finely divided state, and gradually becomes aggregated into larger masses. The work of Ostwald† and of Hulett‡ has shown how greatly a difference in size of the grains may affect the solubility, especially of a salt only slightly soluble.

The latter explanation seems the more probable for several reasons. In the first place, no sharp change in the solubility has ever been detected, such as would be expected from the appearance of a new, more stable solid phase. Again, the difference between the specific gravity of the flocculent precipitate and fused horn-silver is very slight, and their heats of solution in cyanide are identical, indicating little or no difference of molecular constitution between the two.|| Moreover, as will be shown later, the curdy precipitate may be successfully washed in a measure unattainable with crystalline powders, showing that the innermost recesses of the solid are more than usually accessible, and therefore that the structure is very finely divided and loosely knit. The more compact, less soluble precipitate, obtained either by heating or by long standing, has largely lost this possibility of being thoroughly washed, and has become also much less soluble—facts which are quite in line with the above hypothesis. However this may be, the uncertainty of the solubility is a fact of important significance to the analyst, for it obliges him to determine the amount of solution in every experiment—the solubility can never be assumed as known.

The matter is yet further complicated by the well-known fact that the presence of excess of either ionized silver or ionized chlorine causes a depression of the solubility, in the manner demanded by the law of concentration effect.§ A large excess of either precipitant reduces the solubility to so small a value as to be practically negligible

*Ostwald, Z. phys. Chem., **22**, 307, (1897).

†Ostwald, Z. phys. Chem., **34**, 495 (1900).

‡Hulett, ibid, **37**, 385 (1901); **47**, 357 (1904).

||Laevinsohn determined the specific gravities. His results were verified and the thermo-chemical argument added to them by Dr. W. N. Stull and one of us, in some work not yet published.

§Hoitsema, Z. phys. Chem., **20**, 272 (1896).

in most cases.* This may indeed be the reason why the precipitate appears in a form so loosely knit, for at the moment of precipitation it is almost impossible that the two precipitating liquids should for more than an instant be exactly equivalent. Hence each first particle of precipitate would quickly be surrounded by a liquid unfavorable to its union with another in compact crystalline fashion.

Mulder thought that an excess of either silver or chloride equivalent to four times the weight of the dissolved argentic chloride was enough to complete the precipitation, and Stas thought that exactly three times the equivalent amount sufficed. It is clear now that this limit is determined merely by the efficiency of the means used to detect the last faint cloud of precipitate, and then only approximately.

As has been said, the changing solubility demands that every filtrate be tested quantitatively. The methods which may be used are all open to some criticism. The determination of electrolytic conductivity is in vain when any other electrolyte is present, and its interpretation is complicated even in pure aqueous solution by possible hydrolytic complications. The determination of electromotive force depends upon the rigorous application of the law of concentration effect to electrolytes—a somewhat doubtful question. The actual evaporation of the solution and weighing of the precipitate leads to many errors when silver is in excess,† and the determination of the intensity of the opalescence upon precipitating the dissolved chloride depends greatly on the details of the production of the opalescence.

From among all these methods we chose the last, after a very careful study of their probable errors. But although fairly confident of its results, for reasons shortly to be given, we were careful in every case to allow in each experiment as little dissolved argentic chloride as possible, so as to reduce the possible error to a minimum.

The method of comparing the intensity of the cloudiness of opalescent solutions and therefore the quantities of suspended precipitate has already been discussed at some length in a recent paper on the nephelometer.‡ This instrument consists of a device for the comparison of the tint or brightness of two solutions containing precipitate, viewed against a dark background. By making one of these opalescent mixtures from a known amount of material, an unknown amount may be estimated by comparison with it. It is easy to show that

*Compare page 30.

†Richards, Proc. Am. Acad., **29**, 71 (1893).

‡Richards and Wells, Am. Chem. Jour., **31**, 235 (1904).

with this instrument the average of many results is within 1 or 2 per cent of the truth, so that the error with 2 milligrams of dissolved argentic chloride is probably less than 0.04 milligram. This degree of accuracy is as great as can be obtained in the collection of a precipitate for weighing, hence the method is to be ranked among those suitable for exact work.

With the perfected nephelometer it was possibly to study the progressing precipitation of very dilute argentic chloride in a way previously impossible, and several unexpected irregularities were found during its course. Since these are important in the quantitative sense, they must all be briefly discussed.

The most striking of these is the variation in the time of complete precipitation caused by the presence of electrolytes. For example, a solution of argentic chloride, on adding a slight excess of soluble argentic salt, becomes opalescent far more quickly in the presence of much sodic nitrate or nitric acid than in the absence of such an electrolyte. At the end of five minutes the former solution appears about three times as cloudy as the latter; and several hours are needed for the two solutions to attain equality of opalescence at a maximum value, which thereafter remains constant. It appears from this fact that the precipitate probably at first forms in a colloidal state, since electrolytes are known to hasten the precipitation of colloids. This inference is confirmed by the occasional appearance of pale blue or pink tints in the incipient precipitate, which disappears as the cloudiness becomes more intense.

Oddly enough, a solution of pure argentic chloride (made by shaking the curdy precipitate with water and filtering) attains its maximum cloudiness after subsequent addition of argentic nitrate more rapidly than a solution of similar dilution made by mixing equivalent amounts of very dilute argentic nitrate and sodic chloride solutions. The trace of sodic nitrate left in the latter case seems to be unable to counteract some other tendency holding the precipitate in solution. At first it seemed possible that minute invisible "crystal germs" might be present in the filtered solution, which accelerated the appearance of the opalescence, but this surmise was soon overthrown experimentally. A solution made from curdy silver chloride and found nephelometrically to contain 1.28 milligrams per liter, was diluted with an equal bulk of pure water, and its concentration after agitation for over one hour was determined by the nephelometer. The average concentration found by five trials, 0.61 milligram per liter, agreed with that expected within a reasonable limit of error, and moreover the speed of precipitation was no less than before. There could hardly have

been any "crystal germs" existing in the more dilute solution, hence one must assume that the undissociated part of the argentic chloride is really in a different state, when it is dissolved out of salt long formed from that in which it is when in the act of precipitation. The observation at least adds one more anomalous fact, perhaps giving a clue to some of the other anomalous facts, concerning the solubility of argentic chloride.

The application of these observations to the nephelometric analysis of a very dilute silver chloride solution is obvious. It is a difficult matter to prepare a standard which will behave in exactly the same way as the solution to be estimated. By adding appreciable quantities of nitric acid to each, it is nevertheless possible to hasten the precipitation of each so greatly as to cause them to proceed at a speed almost equal; and the maximum cloudiness thus quickly attained persists unchanged in relative intensity for hours. It seems highly probable that the result thus reached really represents the amount of dissolved argentic chloride; especially because the same result is attained after a much longer time even when no electrolyte is present.

The actual extent of the solubility of argentic chloride thus estimated varied through wide limits, as has already been stated. For the solution freshly filtered from the curdy precipitate in the usual condition at 20° the amount dissolved was ordinarily about 1.5 milligrams per liter, a result about equal to that of Kohlrausch and Rose and others. On long standing such a solution was found to decrease in concentration, on one occasion to as little as 1.1 milligrams per liter, although no visible precipitate was seen on the glass. The trace of material represented by this difference was probably adsorbed by the glass. This observation points out the necessity of determining the strength of an unknown solution immediately after its filtration, a precaution which was carefully heeded in the quantitative part of the work.

Although sodic nitrate and nitric acid hasten the precipitation of the curdy opaque form of argentic chloride, they augment slightly the amount which finally remains in solution. By means of the nephelometer it was found that a saturated solution of curdy argentic chloride in the presence of about tenth normal sodic nitrate and a small amount of nitric acid usually contained as much as 3 milligrams of the slighly soluble halide per liter. A mixture of this type was present at the conclusion of each nephelometric experiment recorded in the experiment on the ratio between sodic chloride and silver, and the bearing of the actual value on the investigation will be there discussed.

The solubility of silver chloride in a liquid containing a large excess of one of its ions has been stated to be "practically negligible in most cases" (p. 27). In determining the ratio between silver and silver chloride, however, it seemed advisable to determine even this solubility, which may partly represent the solubility of the undissociated silver chloride, as distinguished from that ionized, and also includes the slight correction for the imperfect retaining power of even the best filters. The fact that a single part of silver chloride may be detected in 30,000,000 parts of water by the nephelometer in the presence of an excess of silver nitrate shows the approximate order of this solubility.*

In five experiments, in which silver chloride was precipitated by an excess of hydrochloric acid, the combined mother liquor and wash waters remaining after filtration were evaporated to dryness. The residue was taken up with a very small quantity of ammonia and then neutralized with nitric acid. After the addition of a slight amount of sodic chloride, the silver chloride was estimated by the nephelometer, by comparison with tubes made up with known amounts of silver in the same way.

Silver chloride found.

In 3 liters	0.09 mg. AgCl.
In 3 liters	.13
In 3 liters	.05
In 2 liters	.05
In 2 liters	.05
Mean	.03 mg. per liter

This value represents the solubility of argentic chloride in water containing sodic nitrate and an excess of hydrochloric acid, together with those traces of the substance which could not be collected upon a filter. It is not certain that the same value would be obtained if it were possible to determine this infinitesimal solubility in the presence of an excess of argentic nitrate; but the fact that the limiting value previously found by one of us is about of this order seems to render this probable. Hence, for the sake of completeness, the correction was applied to the results in the latter case as well as in the former, although it was so small as not even to affect the third decimal place of the atomic weight of sodium.

Further consideration of the solubility of argentic chloride will be given in other appropriate places.

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*Richards, Proc. Amer. Acad., **29**, 74 (1893).

THE OCCLUSION OF DISSOLVED SUBSTANCES BY ARGENTIC CHLORIDE.

It is well known that all precipitates have a tendency to carry down with them other substances from the solution in which they are formed.* According to the nature of the precipitate, the mechanism of this contamination varies. A basic precipitate such as ferric hydroxide is likely to carry down traces of acid in the form of basic salt; an acid precipitate such as silica is likely to carry down traces of base; many substances are contaminated in the act of precipitation by the admixture of isomorphous substances in solid solution; all or nearly all crystals contain within themselves minute cells inclosing mother liquor; and very finely divided precipitates, because of their large surface, pertinaciously adsorb in varying amount impurities from the supernatant solution. Obviously contamination from any of these sources must be scrupulously avoided in accurate work, and the peculiar qualities of each precipitate under investigation must be studied.

As has been said, argentic chloride was known by Stas to occlude argentic nitrate, which is easily detected by its blackening effect upon fusing the contaminated chloride.† This test is a delicate one. Stas found that upon working with solutions of argentic nitrate weaker than decinormal, the occlusion was so slight as to be negligible; therefore in his early experiments he took great pains never to use solutions stronger than this. Later he seems to have overlooked this precaution, since he used much more concentrated solutions. Although realizing that argentic nitrate is occluded by the precipitate, Stas seemed never to have guessed that other salts might also be taken up in this way. Evidently the question was one which needed further investigation, and the outcome of the investigation is recorded below.

It was convenient at first to determine whether or not the occlusion of sodic nitrate or sodic chloride would also affect the appearance of the silver salt on fusion, in order to discover an easy qualitative test for the presence of either. As a matter of fact, the former salt was

*Jannasch & Richards, J. Prkt. Chem., **39**, 321 (1889) Schneider, Z. phys. Chem., **10**, 425 (1892); Richards, Proc. Am. Acad., **35**, 377 (1900); Z. phys. Chem., **46**, 189 (1903).

†Richards, Proc. Am. Acad., **29**, 76 (1893). The blackening occurs in full measure only when the argentic nitrate is occluded from aqueous solution. Perfectly dry argentic nitrate fused with dry chloride is but slightly decomposed, and the fused mass is merely gray, not black. The probable explanation is obvious.

found by actual admixture to color the fused silver chloride a pale buff, rendering it opaque; while the latter had no perceptible effect upon its appearance. Thus Stas could not have detected the presence of sodic chloride in his precipitate by the appearance, whether fused or unfused. An impurity of argentic nitrate being thus the most easily detected among the possible impurities, the next step was to use the contamination with this salt as a means of testing the properties of the precipitate.

It was early found that upon shaking pure argentic chloride with a solution of argentic nitrate, the latter is adsorbed upon the surface of the precipitate. If a solution containing argentic nitrate and the curdy precipitate is divided into two equal volumes, one containing the precipitate and one clear, and if the precipitate is then carefully washed, more argentic nitrate will be found in the portion which contained the precipitate than in the other portion. A further evidence of this adsorption is found in the fact that the theoretical amount of washing is especially inadequate to remove the last traces of adhering electrolyte.

These experiments show not only that the nitrate is adsorbed, but also that some at least of the adsorbed salt may finally be washed off.

In view of this result, it seemed probable that the reason why silver chloride occludes silver nitrate in the act of precipitation is because the former adsorbs the latter during this process, and the adsorbed material is then covered up by newly-formed precipitate. The more dilute the precipitating solutions, the less considerable would be the adsorption.

The peculiar curdy, flocculent form of this precipitate suggested that since the material is so flexible, long-standing and gentle agitation with pure water might allow the occluded material to escape, although from a more rigid precipitate this escape is known to be impossible. With this possibility in view, a number of experiments were made in the following manner: Argentic chloride was precipitated from several portions of a concentrated solution of the nitrate, thus occluding much (in some cases as much as 0.1 per cent) of this salt. The effort was then made to wash these precipitates; and the possibility of thorough washing was found to vary greatly with the treatment of the precipitate. In those cases where the precipitate had remained for two or three days in contact with a mother liquor rich in silver, it was found much more difficult to remove the nitrate than in cases where the washing was more prompt. It seems as if the innermost cells of the precipitate are closed upon standing during the well-known contraction which then occurs. In one case where normal solutions had been used in precipitation, six prompt, gently-agitated washings with pure water were enough to remove practically

all the occluded material and yield a chloride which fused without blemish; but this praiseworthy behavior was the exception rather than the rule. In this case the innermost cells must have been cleaned before they closed during the compacter aggregation of the precipitate; but usually traces of silver nitrate were inclosed, and when they were once inclosed were beyond the reach of even a dozen washings. Therefore more dilute solutions of argentic nitrate were used in precipitating, in order to find the limit beyond which a satisfactory precipitate was certain. Third normal solutions were found to be still slightly too concentrated, but fifth normal solutions always yielded a satisfactory result, if speedily but gently washed six times, and then occasionally agitated in pure water in order to dissolve out the last trace of nitrate. In previous determinations in this laboratory still less concentrated solutions (tenth normal) were used, so that no correction need be applied to those determinations on this account.* This further dilution is necessary unless the curdy precipitate is speedily washed or agitated with a solution containing no excess of silver.

Having thus obtained light on the mechanism of the occlusion of argentic nitrate, we turned our attention to the possibility of occluding sodic chloride. Here, as had been said, no qualitative experiment can conveniently prove the presence of the impurity. Hence recourse was had to a quantitative experiment. An amount of pure salt known by previous experiment with very dilute solutions to be exactly equivalent to a given weight of pure silver was carefully weighed out, and the solid was dropped into a fairly concentrated solution of the nitrate, according to Stas's later method of procedure. After two hours' thorough shaking and a day's standing, which Stas had always given, it was found that 0.014 per cent more of salt had to be added in order to attain exact equivalence, showing that this amount of salt remained occluded by the precipitate even after the shaking and standing. Agitation for another day leached out about one-half of the occluded salt, but seven days' soaking and agitation were required before the full amount (0.014 per cent) of extra silver nitrate was needed to attain equivalence with the salt dissolved out of the precipitate. Subsequently in several days no more salt appeared, hence the final condition must have been reached. Since probably some silver nitrate also was occluded, it is clear that these figures represent a minimum value, and the certain error introduced by Stas's method of procedure

*See for example, Richards, Proc. Am. Acad., **29**, 76 (1893).

was demonstrated. The reason why he obtained consistent results was simply because he used exactly the same method in each analysis.

Obviously, then, a solid salt is not to be dropped into a precipitating solution—indeed, such a proceeding is so repugnant to the instinct of a precise quantitative analyst that it is surprising Stas should have been guilty of it. But how dilute must the precipitating sodic chloride be in the present case in order to avoid the danger? Careful experiments showed that with fifth normal solutions, as in the case of silver, such slight occlusion as existed was quickly removed by gentle agitation, and after a short time the mixture showed a constant equilibrium point. Hence in our final experiments the solution was always as dilute as this. In previous similar work in this laboratory, the solutions of halide were rarely stronger than fifth normal, and never much stronger, so that the error from this source must have been very small.

It might be supposed that when the sodic chloride and argentic nitrate are too dilute to be carried down with the precipitate, sodic nitrate is not likely to be carried down in important amounts. For if both silver and chloride are fifth normal, the resulting sodic nitrate must be tenth normal, a dilution at which even silver nitrate is not sensibly occluded. Nevertheless, as a matter of fact, the final experiments yielded quantitative evidence of the occlusion of a trace of this salt, amounting to 0.005 per cent of the weight of the precipitate. This is probably because the precipitate was obliged to stand for some time in the solution, and it is doubtful if this source of error could be wholly avoided.

From these experiments it appears that the degree of dilution at which occlusion ceases to be seriously troublesome is about the point at which most physical chemists agree that the realm of dilute solutions begins. Hence it would seem that in these cases of adsorptive occlusion the undissociated salt is that which is occluded, in confirmation of other work.*

Obviously the occlusion of argentic nitrate, or of sodic chloride, would affect the results of the analysis, no matter whether silver or argentic chloride served as the weighed standard wherewith to compare the weighed sodic chloride, although more seriously in the former case than in the latter. On the other hand, the occlusion of sodic nitrate could only affect the result when the argentic chloride was weighed; its occlusion would have no effect on the amount of silver required to precipitate the chlorine. The possible effect of these disturbing influences will be alluded to again during the recital of the quantitative operations.

*Richards, MacCaffery, and Bisbee, Proc. Am. Acad., 36, 377 (1901).

It is needless to say that these experiments were carefully carried on in complete darkness, in order to avoid the known disturbing effect of photochemical action. The temperature was usually 20° C. Undoubtedly this condition is important, since the aggregation of argentic chloride is greatly affected by change of temperature.

THE RATIO OF SODIC TO ARGENTIC CHLORIDE.

Two obvious means are available for determining the combining weight of sodic chloride—one, by weighing the amount of argentic chloride which may be made from a given weight of this salt; the other, by discovering the weight of silver needed to precipitate all its chlorine. Both these methods involve a consideration of all the special points mentioned in the preceding sections, and both are essentially gravimetric, although both involve the use of the nephelometer in order to estimate the last traces of silver or chlorine in the supernatant liquid.

The actual investigation of these two methods proceeded simultaneously in order to economize the time during the long delays to which each was frequently subject. Indeed, in some of the previous work in this laboratory, where the pure materials were scarce, the two methods were actually combined in the same analysis, by first determining the weight of silver needed to precipitate the chloride, and then weighing the chloride produced. This last procedure is nevertheless somewhat objectionable on account of its complication. It is moreover subject to slight opposing errors; the avoidance of one of these involves the admission of the other, as has already been pointed out in a preceding communication.* The magnitude of the uncertainty thus caused is not great, and the final error involved is insignificant even in atomic weight investigation of ordinary caliber, usually not exceeding 0.01 per cent; but in the present case extraordinary accuracy was sought. Hence, although the methods were studied simultaneously, they were never combined in the same analysis. For this reason the work is easily divided into two sections, each treating one of the two ratios named above. Of these it is convenient to discuss first the ratio of the chlorides to one another; and this discussion is taken up in the present chapter.

After the preliminary experiments had indicated the nature of the problems involved, a single specimen of pure sodic chloride was used for analysis until all the details of analysis were perfected. Then the

*Richards and Archibald on the atomic weight of cæsium. Proc. Am. Acad., 38, 443 (1903).

various samples of salt were analyzed by methods of known precision. The temptation to vary two conditions in a single new experiment is thus easily avoided. The detailed description of every step of the analytical process follows.

It was soon found that salt when free from excess of acid can be fused in a platinum crucible in the air, without either attacking the crucible to an important extent, or becoming appreciably alkaline. Quantitatively, it was later proved, as will be shown, that salt thus prepared is identical to that fused in a platinum boat in a vacuum and transferred and weighed in the familiar "bottling apparatus" which has served so conveniently for hygroscopic substances. It was found, moreover, that a crucible full of salt thus prepared did not gain in weight during the operation of weighing, on account of the dry winter atmosphere of the steam-heated weighing room. Probably this would not have been the case in a moist climate; but being the case, it facilitated greatly the present work.

The crucible generally used for fusing the salt was, of course, previously freed from iron, and during twenty-three fusions it lost only 0.47 milligram, or 0.02 milligram each time. It is possible that a portion of the weight was lost by volatilization during the preliminary ignitions of the crucible, when it was being prepared for weighing alone; but probably most of this trace of platinum went into solution in the salt. The weight of the crucible before fusion was always taken as the true one, however; therefore even this slight possibility of loss of course could not affect appreciably the quantitative result.

During the fusion of the salt the crucible was inclosed in a larger covered Berlin porcelain crucible, especially made to fit it, and heated by a blast lamp in a small clay furnace. The products of combustion were suitably deflected, so that only pure air should be in contact with the salt in the crucible. The fused salt was cooled in a desiccator in the balance room, and the weighing was conducted by the substitution of a suitable tare-crucible, as usual.

In order to avoid all risk of accidental loss, the salt was dissolved from the crucible by placing it in a large covered beaker, and after covering it carefully with water, agitating it gently from time to time until solution was complete. This solution thus carefully prepared was transferred to a 2-liter Erlenmeyer flask with a well-ground glass stopper, where it was diluted to suitable volume (over 5 liters per mol). Here it was precipitated by the at least equally dilute argentic nitrate in excess. The precipitate was freed from the supernatant mother liquor by filtration as soon as it had cleared enough to make this separation possible. Promptness is needed in order to avoid the

permanent occlusion of sodic and argentic nitrate in the manner already stated, but too great promptness prevents complete precipitation of the silver halide. About fifteen hours was usually allowed for the settling of the solution. Agitation is not necessary.

The clear supernatant liquid was decanted through a large, carefully prepared Gooch crucible. The mat of this Gooch filter, through which all the mother liquor and wash waters were passed, was prepared of selected fibrous asbestos shreds, which had been boiled with nitric acid and well washed. The mat was a trifle thicker than a filter paper—so that the holes of the crucible were indistinctly visible, when viewed in front of a strong light—and was not allowed to extend up the sides of the crucible. A preliminary ignition of the mat was found to result in a slight disintegration and brown coloration, and caused loss during washing; therefore before weighing the mat was dried at a lower temperature, namely, about 150°. This same temperature was used later in drying the argentic chloride. During the operation of washing at first all but a trace of the precipitate was left in the flask, and it was then rewashed by decantation. After each washing, the precipitate was allowed to drain several minutes, for silver chloride is known to hold water like a sponge. At the second or third washing a disintegration of the precipitate often took place, resulting in an emulsionlike mixture, but in most cases this could be prevented by the presence of a little nitric acid. The precipitation had been made with silver nitrate in excess. The first three washings of 0.2 liter each were made with very dilute silver nitrate, and this was displaced in the fourth washing by about 0.05 liter of pure water. In such wash waters, which, with the mother liquor, usually amounted to about 2 liters, no trace of chloride could be found by the nephelometer. The main weight of silver chloride was corrected by + 0.06 milligram, however, in every case, for the otherwise determined solubility in such wash waters (p. 30). From five to eight subsequent treatments with pure water, very slightly acid, in 0.1 liter portions, completed the washing. These later wash waters were treated in the manner described below, in order to determine the chloride which they always contained.

The precipitate was now transferred to the filtering crucible wholly by means of a stream of water. It was found convenient first to transfer and pack down by air pressure a small portion of the precipitate on the asbestos mat, in order that the greater part of the argentic chloride might be easily separated from this mat for fusion. By resting the lip of the flask on the Gooch crucible it is possible to direct a stream of water from a wash bottle into the flask and finally wash out

every particle of precipitate. In the most careful experiments the wash bottle was provided with protecting bulbs to preserve the purity of the water, or was dispensed with altogether, being replaced by a jet driven by hydrostatic pressure. At this stage the cloth covering was necessarily removed from the flask. The flask was finally rinsed with ammonia, which was carefully tested for a possible trace of silver chloride.

On drying the precipitate the temperature was made to rise very slowly above 100° during two or three hours. This deliberate drying was found to be more effective than the immediate application of high temperature, presumably because a hard coating was not then formed about the mass of the precipitate. Finally the temperature was maintained at about 150° for two or three hours longer. In this way fairly constant weight is easily attained, which fifteen hours' further heating at 150° changes very slightly. The last traces of water were always expelled by fusion, as is described below.

In many of the experiments the silver chloride was dried in an electric drying oven heated by hot platinum wires conveying a current of an ampere or two.* When properly constructed this oven gives very satisfactory results. The working of the oven is somewhat more satisfactory if the platinum wires are not heated to redness. In some of the later experiments the precipitate was dried in a clean copper oven heated by a gas flame with no apparent difference in result.

The precipitate thus collected and dried was carefully weighed and then freed from adhering asbestos and transferred to a weighed porcelain or quartz crucible for fusion. The crucible and contents were tared against a similar crucible and contents, and the argentic chloride under examination was then fused in a clean oven constructed from a large porcelain crucible, from the interior of which the products of combustion of the gas were carefully deflected. The fusion is necessary, because minute drops of water are always held by the hardened argentic chloride in sealed cells. It is true that the loss on fusion is not great, never amounting to 0.01 per cent of the weight of the precipitate, but it was enough to receive consideration. In every case it was determined and the appropriate individual correction applied to each weight. The maximum value of the correction was 0.008 per cent and the minimum 0.003 per cent. That the loss was not due to volatilization of silver chloride is easily shown by the invariability of the weight upon fusing a second time. That it was not due to accidental reduction was shown in the later experiments by fusing again in a

*Richards, Am. Chem. Journal, **22**, 45, 1899.

stream of chlorine, when the mass gained on the average only 0.001 per cent. The fused argentic chloride, even before its treatment with chlorine, was usually pearly and colorless.

In any case, it is clear that this loss on fusion, which has been rejected as of doubtful significance by some authors,* really represents included water, and must be heeded.

The determination of the weight of the main mass of the precipitate having been thus determined, attention must be directed to several other precautions necessary to insure exact work. In the first place, all the liquid which has passed through the Gooch crucible was passed through a small washed filter, in order to collect the minute asbestos shreds which even the best fibrous asbestos seems to lose under pressure. This was done as soon as possible after filtration and before proceeding to solubility determination. A siphon filtering arrangement, or a large inverted flask fitted with a carefully cleansed rubber stopper with two tubes arranged so as to maintain constant level, obviated the tedious process of filtering by hand. The little filter was finally washed free from salts, and the weight of the ignited residue (minus the filter ash) added to the weight of Gooch crucible and precipitate. This residue usually amounted to only one or two tenths of a milligram. Observation in the microscope easily showed that the residue was really asbestos.

Because it was the object of the research to test every step of the processes involved, the loss and recovery of asbestos shreds was tested by special blank experiments. Large volumes of water were passed through empty Gooch crucibles provided with the usual mats; and the loss of each crucible after drying was found, as well as the weight of shreds recovered from the filtered water. Below are given the results of these blank experiments:

	Loss of crucible.	Asbestos found.
1.	0.00034	0.00034
2.	.00016	.00045
3.	.00019	.00016
Average..	0.00023	0.00032

In two of these experiments the loss very nearly equaled the amount of asbestos found; the other one must have been contaminated by an accidental outside impurity; but the results of the blank experiments are enough to show that the correction is a real one and not to be omitted.

*Scott, J. Chem. Soc. Trans., 79, 147 (1901).

In most experiments the residue of asbestos shreds was found, after ignition, to contain a trace of silver. This was undoubtedly produced from the decomposition of silver chloride during ignition, the latter salt having passed through the Gooch as exceedingly fine particles or having precipitated, in time, upon the asbestos shreds. The amount of this silver, as well as the amount of asbestos shreds, varied according to the efficiency of the Gooch mat and the fineness of the holes of the Gooch filter—the smaller those holes, the better. The loss of chlorine upon ignition was determined in sixteen experiments, chiefly in those upon the synthesis of silver chloride. This was done by determining the trace of reduced silver by Volhard's process, using $\frac{1}{100}$ normal solutions. The average of determinations, which varied from 0.00 to 0.07 mg., amounted to only 0.02 mg. This correction was applied. Although negligible, its magnitude had to be determined in order that one might be assured of safety in neglecting it.

With the asbestos at our disposal, the prepared Gooch crucible was not at all hygroscopic. An hour's standing in the balance case had no effect upon its weight. Even upon ignition, the mat, weighing less than 0.03 gram, lost only a negligible amount—and it was never heated above 150° in the actual analyses.

As has already been said, no chloride could be found by the nephelometer in any of the wash waters containing any considerable amount of argentic nitrate. Hence, after filtration through the small filters, these were cast aside and the small solubility correction of 0.03 mg. per liter applied to them.

The next two or three wash waters containing only small amounts of nitrate were collected separately, because they contained traces of chloride also. The subsequent wash waters, free from nitrate but containing much chloride, were all united. The chloride in both separate portions was carefully determined by means of the nephelometer—that is, by comparison of opalescence. The two portions, one containing traces of argentic nitrate and one free from salt, must be estimated separately, because if all the wash waters are mixed together the opalescence usually occurs prematurely, a circumstance which interferes with the accuracy of the nephelometric comparison.

The amount of silver chloride thus found in the wash waters was added to the weight of that collected on the Gooch crucible.

Any accidentally included foreign substance—for example, silica from the glass-stoppered flasks, dust from the air, or occluded sodic nitrate—which would make the obtained weight of silver chloride too great, would make the computed atomic weight of sodium too low. Since our results were lower than Stas's, particular attention was paid

to these and similar possibilities. One question especially seemed to demand an answer, namely, that concerning the possibility of the abrasion of powdered glass from the ground-glass stopper of the precipitation flask.

A newly ground stopper sheds glass noticeably. It must always be polished and rubbed a long time until the loose particles are thoroughly dislodged. A flask of soft glass never ceases to grind away slightly every time the stopper is inserted. The large 2-liter Erlenmeyer flasks used in the final experiments were of very hard insoluble glass, with rather wide necks, very suitable for precipitation and for washing. In order to test the extent of their abrasion, one of the stoppers was removed and replaced a hundred times. The resulting powdered glass was collected on a small fine filter and found to weigh 0.2 mg. Since, during a single determination, the stopper was not replaced over a dozen times, it is safe to infer that the error from this cause could not have exceeded 0.02 mg.—a negligible quantity.

Other sources of contamination were so carefully guarded against that they can hardly have been present.

The foregoing general description may be profitably illustrated by recounting the details of a single experiment, before the results of all the experiments are given.

EXPERIMENT 63.

April 5, 1904. Salt J.

	Grams.
Corrected excess weight of crucible over counterpoise.....	0.19994
Corrected excess crucible plus fused salt over counterpoise...	5.76754
Weight salt in air (24°, 764 mm.).....	5.56760
Vacuum correction.....	+ 0.00231
Weight of sodic chloride in vacuum.....	5.56991

As a suitable excess of silver nitrate, 16.40 grams were taken for precipitation. The concentration of the silver salt being about fifth normal and that of the sodic salt not much greater, the total mother liquor was 1.4 liters. Five washings of the precipitate were made after it had stood over night, with 0.2-liter portions of water containing about 0.05 gram of silver nitrate per liter. Washings Nos. 6 and 7 were made with pure water and collected separately. Washings 8 to 12 were made with slightly acidified water and collected separately. The whole precipitate was finally washed upon the Gooch crucible. After drying it appeared perfectly white.

	Grams.
Corrected excess weight Gooch crucible (dried at 150°) over counterpoise	0.21709
Corrected excess weight crucible and AgCl (dried at 150°) over counterpoise	13.87382
Weight of silver chloride in air	13.65673
Vacuum correction	+ 0.00100
Weight of unfused AgCl in vacuum	13.65773

The mother liquors and wash water were passed through a small filter, which was ignited in a small porcelain crucible.

	Grams.
Corrected excess porcelain crucible over counterpoise	0.42525
Corrected excess, plus residue and ash	0.42535
Residue and ash	0.00010
Ash	0.00001
Residue, asbestos shreds	0.00009
Loss of chlorine during ignition (see page 39)	+0.00001
Total residue	0.00010

A large portion of the silver chloride, 10.50 grams, was fused in a small approximately counterpoised crucible weighing about 8 grams.

	Grams.
Corrected excess crucible, plus AgCl, over counterpoise*	10.64846
After fusion, corrected excess over counterpoise	10.64769
Loss of 10.50 gm. AgCl on fusion	.00077

Hence loss of total AgCl $= \frac{13.66}{10.50} \times 0.00077 = 0.00100$

The nephelometer revealed no chloride in the mother liquor and first five washings; the correction of +0.07 milligram was applied for this solubility even in the presence of the excess of silver nitrate.

Washings No. 6 and 7, volume 0.220 liter in all, were found to have a trace of chloride, and its amount was estimated by the nephelometer, making comparison with two different standard tubes.

The factor for converting 1 milliliter of standard solution in a nephelometer tube into silver chloride per liter was 0.047.

Standard tube containing NaCl solution.	Time of forming opalescence.	Heights of opalescences appearing equal.		Ratio of heights.	Soluble silver chloride.
		Standard.	Wash waters.		
0.02 cc.	15 min.	30	100	0.30	0.30×0.02×0.047= 0.00028 gram per liter.
0.005	7 min.	100	80	....	1.18×0.005×00.47= 0.00028 gram per liter.
	9 hrs.	100	85	1.18	

*In this case the counterpoise contained no argentic chloride, but in the most careful experiments the counterpoise contained as much of this salt as the test crucible.

For 220 cubic centimeters the weight of dissolved AgCl is $\frac{220}{1000} \times 0.00028 = 0.00006$ gram.

Similarly for washings Nos. 8 to 12 (0.94 liter) was found on the average 0.00146 gram of argentic chloride per liter (the individual determination being 1.47, 1.41, 1.54, and 1.44 milligrams). For 940 cubic centimeters we have $\frac{940}{1000} \times 0.00146 = 0.00137$ gram, and hence the total dissolved silver chloride $= 0.00007 + 0.00006 + 0.00137 = 0.00150$.

Altogether we now have for the total weight of argentic chloride:

	Grams.
Weight of argentic chloride (vaccum) in crucible	13.65773
Asbestos, etc., washed through Gooch crucible	+ .00010
Dissolved	+ .00150
Loss of fusion	− .00100
Corrected weight of argentic chloride	13.65833

Ratio, AgCl : NaCl = 13.65833 : 5.56991 = 100.000 : 40.7803.

Molecular weight NaCl (if Ag = 107.93 and Cl = 35.455) = 40.7803 × 143.385	58.473
Assumed atomic weight Cl	35.455
Hence atomic weight Na	23.018

Most of the following determinations were essentially similar to this, but a few small differences should be noted. In Experiment 27 the eight washings were extended over five days. In Experiment 64, which must be considered as the best single experiment of all, the concentrations were lowered to tenth normal, and twelve washings were made, the first within three hours, the last after a day's lapse. Considerable nitric acid was added to the first seven wash waters. The slightly higher result of this experiment probably indicates diminished occlusion of sodic nitrate.

Three experiments were rejected, two because blackening of the argentic chloride showed that the argentic nitrate in the first wash waters had not been eliminated by the subsequent washing with pure water, and one because of known loss of argentic chloride. These oppositely erring results would have no effect on the final average if they had been included; but in such a table as this it seems advisable to include only results not vitiated by known sources of error. On the following page are given the final data and results of this comparison of argentic and sodic chlorides.

The ratio of sodic and argentic chlorides.

FINAL SERIES.

Exp.	Prep.	Wt. NaCl. (in vac.)	Wt. AgCl. (in vac.)	Parts NaCl equal to 100.000 parts AgCl.
		Grams.	*Grams.*	
13	K.	3.27527	8.03143	40.781
19	B.	5.56875	13.65609	40.779
20	A.	4.18052	10.25176	40.779
22	C.	4.54319	11.14095	40.779
23	D.	1.97447	4.84196	40.778
27	E.	3.97442	9.74547	40.782
61	H.	6.69495	16.41725	40.780
62	I.	2.88692	7.07955	40.778
63	J.	5.56991	13.65833	40.780
64	J.	5.85900	14.36693	40.781
		44.52740	109.18972	Av. 40.780

If the atomic weight of silver is taken as 107.930 and that of chlorine as 35.455, the atomic weight of sodium, calculated from the above average, will be 23.017, a result 0.14 per cent lower than Stas's.

In spite of every effort to detect some error tending to diminish the atomic weight of sodium and thus to cast doubt on this low value, and in spite of increasing precautions and increasing skill in the details of the experimentation, the last results are no higher than the very first one. Hence further prosecution of this method seemed to be of no avail. The reason for the difference between this value 23.017 for the atomic weight of sodium and Stas's 23.048 is best discussed after the results of the comparison of sodic chloride with metallic silver have been detailed.

THE RATIO OF SODIC CHLORIDE TO SILVER.

Since the time of Gay-Lussac, the method of titration has been a favorite way of determining ratios between silver and soluble halogen salts. If the end-point were definite, this method would be capable of extreme accuracy. It involves no transference, collection, or weighing of a precipitate; consequently the introduction of silica or alkali from a glass-stoppered flask, occlusion of sodic nitrate, loss of asbestos, and other sources of error, are altogether avoided. After weighing the factors in the proper proportions, dissolving and precipitating, one has only to withdraw a portion of the mother liquor and determine whether or not the true end-point of the reaction has

been reached. It is not strange, therefore, that many eminent experimenters adopted this method in order to determine many atomic weights. The solubility of silver chloride, however, was a fact which Gay-Lussac, Pelouze, Dumas, and many others, as well as Stas in his earlier experiments, did not consider; in consequence, all used the wrong end-point. In his last experiments Stas, recognizing the solubility of argentic chloride, attained the end-point in two ways. The first method consisted in titrating to the extreme limit with sodic chloride and then running back to the opposite extreme limit with silver nitrate; the true end-point was assumed to be half-way between the two limits.* The second method consisted in bringing the mother liquor to such a point that two portions of it gave equal opalescent precipitates with silver nitrate and sodic chloride respectively; this was the end-point established by Mulder. Before accepting this latter method, Stas attempted to prove for himself that a solution of silver chloride in water gave an equally intense opalescent effect with an excess of argentic nitrate and sodic chloride. He concluded that the opalescence in the two cases was identical, but at the same time admitted that the opalescent precipitates were extremely unstable and varied continuously in appearance from the moment of precipitation to the time they had settled out completely.† At first, not hoping to improve essentially in this respect upon the methods of Stas, we used this end-point, and after a few preliminary trials made eight careful determinations, using in all 33.1035 grams of pure salt and 61.0898 grams of pure silver. The atomic weight of sodium calculated for the average of these experiments was 23.032, with maximum and minimum of 23.040 and 23.023, respectively.

These experiments were of value as giving practice in the manipulation, but the extreme variation was so much greater than it ought to have been that clearly some undiscovered cause of variable error was present in the results.

A study of all the possible causes of irregularity eliminated all probabilities except the uncertainty of the end-point. The purity of the salt and the silver left nothing to be desired, for the same samples gave constant results when the argentic chloride was weighed. Occlusion had been precluded by the use of solutions of not much over deci-normal strength, and the mechanical operations were so extremely simple as to leave little opportunity for error. Hence much time was

*Oeuv., 1 755. This is unsatisfactory for many reasons. See Richards, Proc. Am. Acad., 29, 82 (1893).

†Oeuv., 1, 158.

spent in investigating the opalescent phenomena attending the precipitation of traces of argentic chloride. The improved and precise nephelometer* served excellently in this tiresome research. We found that its readings could always be depended upon, and that if any irregularity occurred the fault was with the precipitate within the liquid and not in the means of observing this precipitate.

The first step in these tests was to prepare a solution of pure argentic chloride, free from excess either of silver or of chlorine. For this purpose pure floccy silver chloride was very thoroughly washed in a flask by decantation. From time to time two nephelometer tubes were filled with the clear decanted wash water; to one was added a milliliter of argentic nitrate solution, which contained a milligram of silver, and to the other a milliliter of an equivalent solution of sodic chloride. After stirring, these tubes were examined in the nephelometer within ten or fifteen minutes, and the intensities of the two opalescences were compared. No regularity could be detected in the results, successive trials varying over 50 per cent from one another. For example, in one trial the tube containing an excess of silver was twice as intense in opalescence as the other, while in the following trial, with equal proportions of the same solution, it was only two-thirds as intense as the other. The average of a dozen comparisons confirmed approximately Stas's and Mulder's statement that argentic chloride gives equal opalescence with the two precipitates, but the wide variations between the extremes emphasizes Stas's conclusions as to the uncertainty of the results.

Subsequent experiments showed that the presence of an electrolyte greatly accelerated the formation of the precipitate, indicating a colloidal transition stage. The preceding experiments had been almost free from electrolyte, and in view of this inference, it is easy to see why the formation of the precipitate had been so irregular, for slight differences in the extent and speed of mixing might cause important differences in the coagulation of the colloid. Clearly, in making nephelometric experiments, an excess of electrolyte must be present. Other possible causes of error, such as the effect of light, and the presence of absorbed argentic nitrate or common salt in the precipitated argentic chloride from which the solution was made, were carefully guarded against in the further experiments. In order to avoid possible hydrolysis,† nitric acid was always added.

*Richards and Wells, Am. Chem. Jour, **31**, 235 (1904).

†Mulder, Die Silber-Probirmethode (1859, p. 72). Some of Mulder's observations in this direction may have been due to occluded material, but the danger of hydrolysis is not wholly to be despised.

Even when all these precautions had been taken, however, incomprehensible irregularities were still present in the results. It was then found that the *time* allowed for the formation of the opalescence had not been adequate; that in some cases one tube had clouded much faster than the other, but that in all cases neither tube had attained maximum intensity. Often as much time as eight hours was needed for the attainment of this maximum; but the time must not be too greatly extended, or some of the precipitate will be deposited on the bottom of the tube. The performance of the precipitation when chloride is in excess is thus not wholly parallel with that when silver is in excess, already discussed on p. 28.

In view of these facts, a new comparison was made. A quantity of silver chloride was precipitated in red light from cold decinormal solutions of silver nitrate and sodic chloride, washed twelve times with water weakly acidified with nitric acid and eight times further with pure water, the last washings being made in absolute darkness. Pure water containing such quantities of nitric acid and sodic nitrate as would occur in an actual mother liquor from a quantitative precipitation, was then added, and the mixture was allowed to stand with occasional agitations for a day. In making the nephelometer observations on the decanted liquid, sufficient time was allowed for the precipitates to become constant. Three completely separate trials were made in the nephelometer; and of these are recorded below the depths of liquids which seemed to be equally opalescent.

Observation.	Time.	Tube+$AgNO_3$.	Tube+NaCl.
65	After 8 hours...	98 mm.	100 mm
66	After 8 hours...	100	100
67	After 8 hours...	103	100
Average..	.....	100.3	100

These observations, made with great care, settled every doubt about the correctness of the equal-opalescence end-point. Thus it is clear that Stas encountered difficulties with this method only because he, like all the previous experimenters, did not wait long enough to allow the opalescence really to establish itself in the absence of electrolyte to hasten precipitation.

In the course of these experiments several subordinate points were noted which are worth recording. When the opalescent precipitates were made directly in the tubes from sodic chloride and argentic

nitrate, having first one and then the other in excess, the speed of formation was not like that observed when a solution of argentic chloride was treated with the two electrolytes. In the former case, the maximum opalescence was attained more slowly and the tube containing an excess of chloride always became cloudy much more rapidly than that containing an excess of silver, while in the latter case the difference was much less marked. This adds to the evidence that the dissolved argentic chloride is appreciably colloidal, and that the formation of this colloidal portion requires time.

The possible effect of light upon this end-point was another circumstance of interest, although not of immediate bearing on our quantitative work, since actinic light had been scrupulously excluded. In order to ascertain the effect of light the solution already tested in observations 65, 66, and 67 was agitated in the flask for an hour at a distance of about 30 cm. from a white incandescent electric light. Observations 68 and 69 were made with the mother liquor. It was then agitated in diffused daylight for another hour, an exposure which made the precipitate decidedly bluish, and observations 70 and 71 taken.

Observation.	Tube+$AgNO_3$.	Tube+NaCl.
68	100 mm.	100 mm.
69	100	100
70	97	100
71	100	100
Average.....	99	100

The solution thus gave the same results in the nephelometer as before. Böttger, in his study of the solubility by the conductivity method, also observed that the conductivity did not sensibly alter until the conductivity vessel was exposed to strong light for a considerable length of time. A slight coloring of the precipitate made no difference.* The explanation must be that chlorine thus set free does not ionize. According to Vogel,† silver subcloride is insoluble in very dilute nitric acid. Hence neither an excess of ionized silver nor chloride should appear in the mother liquor. Light, therefore, could not have been the cause of any of the variations in preceding observations, and its complete exclusion had been supererogatory.

*Zeit. phys. Chem., **46**, 521 (1904). †Gilbert's Annalen, **72**, 286.

Having thus, by many experiments, of which those given above are merely samples, assured ourselves that the true end-point may be decided by equality of opalescence when sufficient time is allowed to complete the opalescent precipitation, it became an important matter to make a conclusive series of analyses by this method.

In the first place, a given piece of the purest silver was carefully weighed and was dissolved in a flask upon the steam bath. For every gram of silver about 3 milliliters of nitric acid, of density about 1.20, were used. This density was secured by mixing pure distilled nitric acid of the usual concentration with an equal volume of water. After the silver was dissolved, more water was added and the nitrous fumes were expelled by a brief, very gentle ebullition. A tower of bulbs, ground to fit the neck of the flask, prevented any loss of silver nitrate during the operations. A special experiment proved the efficiency of the bulbs as a means of retaining spray. In this manner of treatment nitric acid always remained in slight excess.

Assuming a probable value for the atomic weight of sodium, the exact weight in air of salt equivalent to the weight of the given piece of silver was calculated and weighed out for fusion. There was always a slight loss of weight when the salt was fused in the platinum crucible, and if, after fusion, more than a milligram of salt was still required, approximately the required amount of well-dried salt was added at once by a platinum spatula. The amount so added never exceeded a few milligrams and its introduction could have caused no error, since in our laboratory salt was not hygroscopic. The exact weight of salt corrected to vacuum was obtained. Any further still slighter lack of equivalence was then made up by volumetric addition of the proper quantity of the same solutions which were to bring the mother liquor to equal opalescences after the precipitation. Of course the recorded weights include all these small additions.

Both salt and argentic nitrate were diluted to a concentration about fifth normal, and were then mixed in complete darkness with all possible precautions, the argentic nitrate being very slowly poured into the salt solution. When in a day or two the precipitate had settled and the mother liquor had become clear, the latter was examined nephelometrically.

It was found to be convenient, in determining the amount of a deficiency of either silver or chloride, to calculate once for all the extent of this deficiency in terms of the ratio of lengths of the two nephelometer columns giving equal apparent opalescence. This was in the first place calculated by means of the law of concentration effect; but practically a slightly different value, based upon experience, was

found to be more accurate. A ratio of 100 millimeters to 80 millimeters was found to signify an excess or deficiency of 0.15 milligram of silver per liter, and other amounts in proportion. Since the average of many readings was probably accurate within 2 per cent and the volume rarely exceeded a liter, it would appear that the end-point was determined within 0.02 milligram of silver. This does not, of course, prove that the results are accurate to within this small margin, because other experimental details may have led to larger error. The difference between the maximum and minimum results corresponds, indeed, to a much greater uncertainty, as will be seen. Hence the end-point is determined precisely enough for our purpose.

The final series of experiments, given below, includes only those experiments in which every known source of error was avoided. In order to illustrate the details of the method, the full record of a single experiment, in so far as it does not repeat what has already been described, is here given.

EXPERIMENT 53.

	Grams.
Weight of sodic chloride (in vacuum) (Sample I).....	5.08685
Weight of silver (in vacuum) (Sample O).....	9.38819

These were dissolved and mixed on February 2, 1904. After two hours' agitation the mixture stood until next day, when an examination was made with the nephelometer. Two test tubes were filled with the mother liquor by means of a clean pipette, withdrawing 0.07 liter for this purpose. The two solutions were very nearly equal in opalescence With occasional shaking the mixture was therefore allowed to stand yet another day, in order to insure the thorough solution of possibly adsorbed material. The subsequent proceedings are summarized below:

February 4 (0.07 liter withdrawn).

Time of standing in nephelometer.	Nephelometer readings.		
	(*a*) Reading of tube with excess $AgNO_3$.	(*b*) Reading of tube with excess NaCl.	$a \div b$.
30 minutes.....	45	54	.83
2 hours.....	43	54	.80
18 hours.....	46	55	.83

This reading indicates a slight deficiency of silver. Hence 0.15 milligram of silver in solution was added to the residual mother liquor, and the mixture was occasionally shaken.

February 8 (0.070 liter withdrawn).

Time.	Nephelometer readings.		
	a.	*b.*	$a \div b.$
5 minutes..	48	30	1.60
16 hours....	60	57	1.05

There was now a slight *excess* of silver. Hence there was added 0.03 milligram of sodic chloride, corresponding to 0.06 milligram of silver.

February 16 (0.07 liter withdrawn).

Time.	Nephelometer readings.		
	a.	*b.*	$a \div b.$
¼ hour.....	50	39	1.28
1 hour.....	50	44	1.14
2 hours	50	46	1.09
12 hours....	53	54	0.98
	36	35	1.03
	55	59	0.93
	33	33	1.00
	70	67	1.04
	52	53	0.98
	37	38	0.97
	24	23	1.04
	360	362	1.00

Thus precise equality had been attained.

Volume liquor now remaining.....	435 cc.
Withdrawn during trials.....	280
Original volume.....	715

If the first addition of Ag had been made to the original total mother liquor it would have been $0.15 \times \frac{715}{575} = 0.19$ mg. Similarly $0.06 \times \frac{715}{505} = 0.08$ mg. Hence extra silver required to produce equal opalescence in original mother liquor $= 0.19 - 0.08$ mg. $= 0.00011$ gm.

Total silver = 9.38819 + 0.00011 = 9.38830 gm. This silver contained 0.0037 per cent of impurity. Weight of pure silver present 9.38795. Then Ag : NaCl = 9.38795 : 5.08685 = 100.000 : 54.185.

Molecular weight NaCl = 107.930 × 54.185, if Ag = 107,930. 58.482
If atomic weight Cl..... 35.455

Atomic weight of sodium..... 23.027

Ten such complete analyses are recorded in the table below.

The ratio of sodic chloride to silver.

FINAL SERIES.

Exp.	Preparations.		Wt. salt. (in vac.)	Observed wt. silver. (in vac.)	Correct wt. of purest silver. (vac.)	Parts NaCl equiv. to 100.000 parts silver.
	NaCl.	Silver.				
			Grams.	*Grams.*	*Grams.*	
41	F.	N.	3.96051	7.30923	7.30896	54.187
44	K.	N.	2.32651	4.29371	4.29355	54.186
46	K.	N.	5.36802	9.90736	9.90699	54.184
45	G.	M.	4.00548	7.39237	7.39210	54.186
47	G.	N.	4.69304	8.66133	8.66101	54.186
52	H.	P.	3.27189	6.03864	6.03842	54.185
53	I.	P.	5.08685	9.38830	9.38795	54.185
55	J.	P.	3.66793	6.76977	6.76952	54.183
56	L.	P.	5.48890	10.13030	10.12993	54.185
57	L.	P.	3.55943	6.56933	6.56909	54.185
			41.42856	.....	76.45752	54.185

The agreement of these results is now as good as could reasonably be expected. Whereas the earlier similar experiments, made before time enough had been allowed for the full development of the opalescence, showed an extreme variation in the results of 0.017, this extreme variation is now only 0.004. Since in these last experiments seven different specimens of salt were used, and three different specimens of silver, it seemed hardly probable that further work in the same direction would add certainty to the average. The chemical identity of the various preparations seems to have been proved.

The atomic weight of sodium calculated from the ratio 100.000 : 54.185, the average of these ten determinations, is 23.027, if silver and chlorine are respectively assumed to be 107.930 and 35.455. This is 0.010 higher than the value obtained by reference to argentic chloride—a difference which seems small in comparison with much quantitative chemical work, but which nevertheless is far greater than the sum of the probable experimental errors of the two series of results.

The conflicting outcome of all these carefully conducted experiments thus still remained not easily explicable. Their value for the atomic weight of sodium differed by over 0.1 per cent from Stas's result, and furthermore, as has just been said, the comparison of sodic chloride with silver yielded a higher result, 23.027, than that found by comparison with argentic chloride, 23.017. Both these discrepancies required explanation before the results could be accepted without reserve.

In the first place, much time was spent in the search for some possible error in our results. For example, several of our samples of salt, especially the preparation numbered K, were tested for lithium with the greatest care by fractional treatment with alcohol. The extreme mother liquors showed no trace of the lighter metal, although in parallel experiments it was found that less than 0.01 per cent of lithium chloride could be detected in this way, even by the simple flame test. This proportion could not affect the atomic weight of sodium by more than 0.002; but since no trace of lithium was found in any of the specimens of our salt tested, it is clear that our low value of the atomic weight could not be due to lithium. The constant results found with differently prepared samples from different sources seemed to exclude the possibility of the presence of the very few other metals which would yield too low a value for the atomic weight, namely, beryllium, magnesium, aluminium, and calcium. Acid could not have been present, since the material was usually prepared from salt finally crystallized from pure neutral solution, and was always fused in air. It gave, moreover, a wholly neutral reaction to methyl orange.

Because no flaw could be found in the operations leading to the new results, the conclusion was inevitable that the old ones were in error. In order to prove this without question, experiments were instituted in which each one in succession of the gravest faults already pointed out in Stas's work were imitated, in order to detect the individual errors introduced by each.

In the first place, two experiments were made in which the salt was prepared approximately according to Stas's method, the substance being fused with ammonic chlorplatinate. The salt thus prepared was compared with pure silver by means of the nephelometer, using, as Stas did, the opalescence which had been given only fifteen minutes to form. In this way 2.67137 and 5.51270 grams of salt needed, respectively, 4.92908 and 10.1717 grams of silver, corresponding to an atomic weight of sodium of 23.039 in each case. Since the value obtained from salt certainly free from platinum in the same way (p. 45)

was 23.032, the difference of 0.007 may probably be ascribed to platinum, which had not been precipitated by thermal decomposition. Presumably, therefore, traces of platinum were present also in Stas's preparations.

In the next place, the effect of the occlusion of sodic chloride by argentic chloride was quantitatively studied. It will be remembered that *Stas always dropped dry sodic chloride crystals into his silver nitrate solution* instead of adding the salt in the dissolved state. Such a procedure offered the maximum opportunity for the occlusion of sodic chloride. In the following experiments, made with the purest material (salt F and silver P) and executed with all the precautions outlined above, this error alone was purposely committed. After dropping in the solid salt, the mixture, having been shaken two hours, was allowed to stand for a day, all according to the manner of Stas. In three experiments (Nos. 42, 51, 48,) 5.37853, 3.34018, and 5.29539 grams of salt required, respectively, 9.92510, 6.16392, and 9.77122 grams of silver, thus giving three determinations of the atomic weight of sodium, as follows: 23.033, 23.033, and 23,036, or, on the average, 23,034.

In the last experiment the gradual dissolving of this occluded salt was shown in an indubitable manner. On continued shaking throughout a week, more and more silver had to be added, until finally the mixture came to complete constancy at a point corresponding to 9.77264 grams of total silver. This quantity gives 23.028 as the atomic weight of the sodium, showing that within a week nearly if not quite all the occluded sodic chloride had been disengaged.

If, then, we sum up the effects which we have found for the three chief errors probably made by Stas in his *later* work, the following result is obtained:

Our value of the atomic weight of sodium from the ratio of sodic chloride to silver	23.027
Effect of too prompt reading of opalescence	+.005
Presence of platinum in salt	+.007
Occlusion of salt in silver chloride	+.007
Result which we should have obtained by Stas's complete method	23.046

This result is so near that found by Stas's assistants in 1881 (23.050) as to make it seem probable that these errors really existed in Stas's work, and that the present investigation avoided them. The acknowledged presence of traces of gas in Stas's silver and silica in in his salt may be neglected in this comparison as being errors of

mutually opposing tendency and almost equal effect. The rectifying of previous work by means of a later correction is always a doubtful process, and the above table is given only to show that Stas's small mistakes have all been traced.

It not so easy to give the numerical magnitude of the correction to be applied to Stas's *earlier* work, which, as has been said, is inconsistent with the later work, because it gives the same result, although a wholly false end-point was used. It is probable, however, that in the early work, carried out by Stas himself, the precipitated argentic chloride was much more thoroughly shaken with its mother liquor than the later work executed by MM. Nyst and Cabilliauw under Stas's direction. Continued shaking would diminish the solubility of the argentic chloride, as well as disengage the occluded salt. Thus the decrease of the latter error might have balanced the effect of a greater error in the end-point, although this in its turn would be less marked than it would have been had the mixture been less thoroughly shaken.

All these considerations tend to support the present determination as against the verdict of the older ones, but no explanation is yet afforded as to the reason for the difference between the values 23.017 and 23.027 found by different processes in the present work. Long consideration of the matter led finally to the conclusion that the accepted value of the atomic weight of chlorine, 35.455, upon which the calculation depends, must be in error. Accordingly this problem also was attacked experimentally. But before these lengthy experiments are recounted brief mention must be made of the successful attack upon another doubtful point, which concerns the sodic chloride.

THE FUSION OF SODIC CHLORIDE IN VACUUM.

This matter has been given an especial heading because it is one which has never before received adequate treatment in an investigation of this kind. It is well known that many substances, when fused in the air, dissolve either oxygen or nitrogen, or both, thereby increasing sensibly their weight. While it was hardly to be expected that this would be the case with sodic chloride, the point should not pass unchallenged in a research striving to attain the highest possible accuracy.

Hence two analyses were made of sodic chloride fused for some time in a platinum boat inclosed in a completely evacuated porcelain tube, and subsequently bottled in dry air in the often described "bottling apparatus." So far as we know these are the only quantitative experiments ever made in which *all* the weighed substances were fused

in a vacuum before weighing. It is true that Stas has shown that ammonic chloride sublimed in a vacuum gave the same equivalent referred to the silver as preparations sublimed in air; but this choice of ammonic chloride had the disadvantage that its two dissociation products possess different rates of diffusion, and moreover his silver had not been fused in a vacuum as ours had been. The data and results are given below.

The ratio of sodic chloride to silver; both substances fused in a vacuum.

No.	Sample salt.	Sample Ag.	Weight. NaCl. (in vac.)	Weight. Purest corrected Ag. (in vac.)	Parts NaCl eq. to 100.000 parts Ag.
59	J.	P.	3.38684	6.25046	54.185
60	J.	P.	4.68529	8.64634	54.188
Average					54.187

These experiments show that probably not enough gas is absorbed during fusion of the salt in air sensibly to alter the apparent combining weight. It is true that gases easily remain in supersaturated solution in liquids, and that long-continued relief from pressure is necessary to remove them; but fused sodic chloride is so mobile and possesses so low a density as to make the retention of much gas very unlikely. That air may be adsorbed by the cold salt is of course highly probable, but the surface of a fused lump is so small that the weight of this adsorbed air must be negligible. One would here expect a lower result from the salt fused in a vacuum, if gas were dissolved in the other experiments, but the results were in fact slightly higher, although not beyond the probable limit of experimental error. It appeared from tests with indicators that the salt remained strictly neutral after fusion in a vacuum, as it did in the air.

Being unable to conceive of any other sensible inaccuracies which could affect the analyses of the chloride of sodium, we turned our attention next to the composition of the chloride of silver, because of the before-mentioned suspicion that Stas was here also in error. An additional reason for this revision is found in the fact that this atomic weight of iodine, found at about the same time, has been found to be about 0.1 per cent too low.*

*Ladenburg, Berichte d. d. chem. Gesell., **35**, 2275. Scott, Proc. Chem. Soc., 18, 112. Köthner and Aeur, Ber. d. d. chem Gesell., **37**, 2536 (1904). Also, Liebig's Ann., 337, 123 and 362 (1904). Baxter, Pro. Am. Acad., **40**, 419 (1904).

THE SYNTHESIS OF ARGENTIC CHLORIDE.

Many accurate analyses were made by Stas which involve more or less directly the atomic weight of chlorine, but of these we are concerned in the present paper only with those which compare silver with chlorine, because such alone could cause an error leading to the discrepancy under discussion. The experimental solution of the problem is thus a comparatively simple matter, to be accomplished by combining silver with chlorine. Among all Stas's experiments there seems to have been only seven which dealt directly with this ratio.* These were carried out by two methods. Of these methods one, the ignition of silver in a stream of chlorine, is acknowledged by Stas to possess errors which he could not wholly correct. Hence the three experiments made by this method are of doubtful value, and only four analyses remain for the purpose of obtaining directly this very important ratio. Even in these the large glass globes employed were more or less attacked by the strong acids or the fused chloride, and, moreover, Stas questioned the purity of the silver used in one case.† There is obviously no doubt of the need of obtaining more light upon this matter.

The fundamental requirements of a satisfactory synthesis of argentic chloride are as follows: First, that the silver must be pure; secondly, that it must all be collected in the argentic chloride, and thirdly, that this argentic chloride must be pure. Because all the error accumulates upon the consequent atomic weight of chlorine and is magnified in calculation, the requirements are usually rigorous.

The fulfilling of the first of these requirements has already been treated in detail, under the discussion of the preparation of silver. Our knowledge of the essentials of this easy but subtle process grew as the quantitative work on the synthesis of the chloride progressed. Whether in the future anyone may be able to discover an unsuspected source of impurity in our purest silver, is of course impossible to say. At least, there can be no doubt that it was of distinctly a higher grade than the silver used by Stas in most of his work.

In order to convert this silver wholly into the chloride without loss or illegitimate gain, two methods were used, for fear that in one of these a constant error might lurk unsuspected. The first consisted in the usual method of solution in nitric acid and precipitation in dilute solutions, being essentially similar to that used in obtaining the ratio between common salt and silver chloride. The weighed silver

*Stas, Untersuchungen (trans. Aronstein) 173, 175 (1867), Ex Oeuvr., 1, 333.
†Stas (Aronstein), pp. 117, Oeuvres, 1, p. 330.

was dissolved with all the precautions used in previous work and precipitated as chloride by hydrochloric acid at concentrations of about fifth normal. Hydrochloric acid was added in excess and the precipitate was washed three times with dilute hydrochloric acid, in order to diminish as much as possible the solubility of the silver salt. After collection on a Gooch crucible, drying at 150°, and washing, the bulk of precipitate was fused in a porcelain or quartz crucible and the loss in weight by fusion determined.

It would appear at first as if the result of this process could furnish nothing not directly calculable from a comparison of the two sodium series, in one of which common salt was compared with silver and in the other with argentic chloride. This is not true, however, for in this previous work the precipitate formed in the presence of sodic nitrate and excess of argentic nitrate, while in the present case an occluded alkaline salt could not be carried down, because none was present, and *all* the silver could be converted into chloride. For this reason the synthesis of argentic chloride in the presence of nothing but volatile substances is an important step in the work.

As usual, in this case also, improvement was effected as the work progressed, and here as before the less perfect tentative work is included in the preliminary table. The synthesis of argentic chloride is a process of greater certainty than a metathetical reaction, for the reasons just stated, and hence finer corrections could be discovered and applied.

These corrections, in addition to the two already heeded, namely, that for the asbestos shreds carried away during filtration and that for the inclosed wash water set free on fusion of the chloride, were five in number.

The first of these was a correction for the presence of a trace of argentic chloride clinging to the collected asbestos shreds. This silver salt lost chlorine on ignition—a quantity which was determined by dissolving the residual silver and titrating with $\frac{N}{100}$ sulphocyanate. The amount of chlorine thus lost on the average was 0.02 milligram in each synthesis—an amount which was added to the weight of the asbestos shreds. This correction might in most cases have been omitted, but it was determined for the sake of certainty.

The second of these corrections was for the slight solubility of argentic chloride even in dilute hydrochloric acid. This solubility may have been only apparent, the trace found being due to the imperfection of even the double filtration through asbestos and filter paper—but in any case it needed determination and correction. The average solubility, from five determinations (page 30), was one part in

30,000,000 of water, which is about the order of the possible solubility of *undissociated* argentic chloride, and hence may have represented that quantity. The determination was made by evaporating the hydrochloric acid solutions, rinsing out the dish with ammonia and testing the resulting solution nephelometrically by comparison with similarly prepared known solutions of silver chloride, as has been said.

The third correction was for an occasional loss of chlorine by the argentic chloride on fusion, owing either to the presence of argentic nitrate or to traces of dust. The darkening thus caused represents a real although often trivial deficiency of weight, but, fortunately, this is easily restored by fusion in a mixture of pure chlorine and hydrochloric gas. Of course this process must not be adopted when argentic nitrate is occluded during the analysis of a metallic chloride, for it would then lead to a large excess of argentic chloride; but it is perfectly safe in the present case. The only suspicion which attaches to it is the possibility that an *excess* of one of these gases might be dissolved. This is undoubtedly a real danger, unless the fused salt is exposed to the air and agitated in contact with it while fused. If this is done, we have assured ourselves by repeated experiments that no essential excess of chlorine remains dissolved.* Two facts pointed to this conclusion—first, that those samples of argentic chloride, which after the preliminary fusion merely in air were perfectly colorless, transparent, and pearly, gained no essential weight on fusion in chlorine (Expts. 80, R. 2 and R. 3, final series, p. 65); and secondly, that argentic chloride fused in chlorine, properly freed from it, and subsequently again and again fused in pure air lost no essential weight.

We always secured elimination of the possible trace of dissolved chlorine by continuing to fuse in air with occasional removal of the cover, and by carefully rolling the inclined crucible around, while held with forceps, during the solidification of the fused mass. Spreading the solid in this way makes it easier to fuse the salt once more without breaking the very fragile quartz crucibles.

The attacking of glass by chlorine in contact with silver chloride and a consequent loss of weight gave Stas considerable difficulty. Baxter has found that even porcelain is attacked in displacing iodine with chlorine in the silver salts. We did not greatly fear a loss of weight of the porcelain crucibles, since our chlorine was dilute, and was applied only for a few minutes; nevertheless we adopted the use of quartz as an added precaution in the later experiments. No difference in results could be detected by its use.

*Dr. Baxter has come to the same conclusion. Proc. Am. Acad., **40**, 432 (1904). And so also have Köthner and Aeuer, Lieb. Ann., **337**, 127 (1904).

A fourth correction which we sought to determine was for the possible volatility of the argentic chloride during fusion. The constancy of weight on repeated fusion, already mentioned, seems to be sufficient proof for considering this correction as negligible. The conclusion is strengthened by the results of Biltz and Victor Meyer, who found argentic chloride to be but slightly volatile at much higher temperature.* It is not, of course, contended that argentic chloride has no vapor tension at 500°, but only that the loss occasioned by its evaporation is too small to receive consideration.

During fusion, however, there is sometimes a slight spurting, or projection upward of minute drops of fused material. Hence the crucible must always be covered with an accurately weighed lid—a precaution which was always taken in the final experiments.

The phenomenon of spurting suggested that weighable quantities of air may be absorbed during fusion in air, and led to our effort to discover a fifth correction. Carefully conducted experiments showed, however, that there was no loss in weight of 3 grams of ordinarily fused argentic chloride when fused again in a vacuum. The fusions were conducted in a porcelain boat, covered with another inverted to serve as a lid. Slight traces of inclosed gas were noticed by Stas in many substances, but our quantitative experiments showed that they do not amount to a weighable quantity either in common salt or silver chloride. Thus, all the final experiments in this paper refer to substances fused *in vacuo*, and hence presumably as free as possible from inclosed air.

There were thus seven possible corrections, besides the correction of the weights to the vacuum standard, which might be applied to the results. Two of these, that for the possible volatility of argentic chloride and that for weight of dissolved air, were so small as to be entirely negligible. The chlorine lost from the traces of argentic chloride clinging to the displaced asbestos shreds was added to the weight of these shreds, and is included therein in the tables below. The three other corrections are recorded in detail in the following tables, which contain the original weight of the precipitate dried at 150° as well as the final corrected values. The almost negligible correction for the solubility of argentic chloride in dilute hydrochloric acid was computed, in the preliminary series, from the volume of the washings.

*Berichte der d. Chem. Ges., **22**, 727 (1889). Köthner and Aeur found a volatilization of only 0.0002 in a case where several liters of gas had been passed over argentic chloride during several hours. This agrees essentially with our result, for the likelihood of distillation in our case was much less (loc. cit., p. 128).

A few inessential changes in the mode of precipitation were occasionally introduced. In Experiments 75, 76, and 79 both solutions were only about tenth normal, and the number of washings was diminished; in R. 1 the argentic nitrate was very dilute, but the hydrochloric acid was somewhat concentrated.

As has been said, the tentative experiments were all classed together in a preliminary series, given immediately below. The table explains itself, for the most part, except perhaps the second column. This defines in the first place the designation of the silver, next the nature of the containing vessel on which it was fused, and last the atmosphere surrounding the metal during fusion. The word "blast" signifies that the sample thus qualified was fused in a blast-flame of illuminating gas and air, delivered from a clean nozzle, and that the resulting mass was cooled in the reducing flame.

Synthesis of argentic chloride.

PRELIMINARY SERIES.

No. of exp.	Description of silver: Sample; support and environment during fusion.	Observed weight of silver (vac.).	First approximate weight AgCl (vac.).	Corrections to AgCl.				Cor. weight AgCl (vac.).	Pts. of AgCl produced from 100.000 pts. Ag.
				Asbestos residue (add.).	Loss on fusion (subtr.).	Gain in Cl_2 (add.).	Cor. for solubility (add.).		
		Grams.	*Grams.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Grams.*	*Per ct.*
65	P, lime, vac.....	9.06483	12.04416	0.10	0.79	0.12	0.06	12.04365	132.861
66	.....	8.39217	11.14987	0.35	0.57	0.14	0.06	11.14985	132.860
70	.....	5.37429	7.14072	0.26	0.51	0.03	0.06	7.14056	132.865
	Average.....	.....	.....	.....	.....	.....	.....	.....	132.862
67	P, carbon, blast	8.08222	10.73844	0.46	0.49	0.22	0.06	10.73869	132.868
68	.....	7.08517	9.41382	0.20	0.50	0.04	0.06	9.41362	132.864
71	.....	7.97715	10.59854	0.45	0.82	0.14	0.06	10.59837	132.859
	Average.....	.....	.....	.....	.....	.....	.....	.....	132.864
72	S, lime, vac.....	8.11978	10.78751	0.36	0.38	0.09	0.09	10.78767	132.857
73	.....	8.53452	11.33904	0.28	0.40	0.09	0.06	11.33907	132.861
74	.....	6.73284	8.94497	0.42	0.51	0.14	0.09	8.94511	132.858
75	.....	8.91366	11.84225	0.48	0.48	0.09	0.06	11.84240	132.857
76	.....	9.72295	12.91736	0.56	0.41	0.09	0.09	12.91769	132.858
	Average.....	.....	.....	.....	.....	.....	.....	.....	132.858
79	U, carbon, H_2..	8.63961	11.47877	0.30	0.61	0.07	0.09	11.47862	132.860
R. 1	V, lime, blast...	11.13795	14.79856	0.24	0.50	0.10	0.09	14.79849	132.865
	Total av.....	.....	.....	.....	.....	.....	.....	.....	132.861
	Stas found.....	.....	.....	.....	.....	.....	.....	.....	132.848

Although not giving the true amount of chloride to be obtained from the purest silver, this table was highly instructive. It showed in the first place that even silver of this grade of purity must be 0.01 per cent purer than that of Stas.* Again, it showed that at least a part of the difference between the two new values for the atomic weight of sodium is due to an error in the assumed atomic weight of chlorine used in the calculations. It proved that the analytical method was capable of yielding very constant results with a given sample of silver (Exps. 72–76). It confirmed previous results† in showing that portions fused in these various ways were not very different, but showed slight variations according to the method of fusion employed. It furnished a means of determining, by later comparison of one or the other of these results with those from the purest silver, the exact grade of purity of the various specimens of silver used in the previous work in this laboratory, in particular that used in the earlier part of the present research. Finally, it furnished sufficient clue to the precautions which must be taken to secure yet purer silver.

A careful study of this table led to the conclusion that a reducing environment is necessary to eliminate traces of oxygen during fusion, and that lime is better than carbon as a support during fusion. The details of this matter have already been described (pp. 22, 23) under the heading "Preparation of Pure Materials," and need not be further detailed here. Suffice it to say that the silver used in the experiments recorded in the table on page 65 was free from the sources of error thus detected.

The final series comprehends ten experiments, made with four samples of silver prepared entirely independently by three different

*There can be no doubt that this difference is due to the fact that Stas fused all the silver used in this part of his work in a porcelain crucible under borax and nitre, thereby introducing both alkali and oxygen (Oeuvres, **1**, 328). His own subsequent experiments (Oeuvres, **1**, 466) showed that this metal was at least 0.005 per cent less pure than his distilled granulated silver, which must, in its turn, have contained some oxygen. His still later elaborate search for oxygen in the silver is not satisfactory, because just before determining the oxygen in it he ignited it in a reducing flame, and because he sought to determine the oxygen only by heating to redness in a vacuum, a process which may have set free only the superficial oxygen. Dumas found 0.008 per cent of oxygen in similar silver by fusion in vacuo (Ann. de chim. phys., **14**, 289, 1878), and Mallet found that silver fused like Stas's purest in the oxyhydrogen blast contained 0.005 per cent of oxygen. (Phil. Trans., **171**, 1020 [1880]).

†Richards, Proc. Am. Acad. **29**, 65 (1893).

experimenters (Dr. Baxter having very kindly given us a piece of his purest silver used in the determination of the atomic weight of iodine, and each of the authors having made separate samples) and two entirely different methods of synthesis.

Of these methods of synthesis one has already been described, namely, the usual method of solution of the silver in nitric acid, precipitation by hydrochloric acid, and filtration on a Gooch perforated crucible. Of course all the precautions and corrections already discussed were applied with as much care as possible. All the vessels used were afterwards washed with a little ammonia, and the washings tested nephelometrically in order to be sure that no silver was lost by adsorption on the vessels. By this method Experiments 69, 77, 78, 80, 81, R. 2, and R. 3 were made. Further unvaried repetition of this process seemed to promise no further light on the question.

Although this method seemed to leave little or nothing to be desired as regards accuracy, it was nevertheless deemed advisable to test it by making a few syntheses by means of entirely a different process, in which all the vessels coming in contact with the precipitate could be weighed. Accordingly a new method was devised, a modification of one of those used by Stas, employing quartz vessels instead of glass. A quartz dish was accurately weighed by substitution of a counterpoise of a similar composition, surface area, and weight. A watch-glass to serve as its cover was weighed in a similar fashion separately. A weighed piece of silver was placed in the dish, which was supported in a large empty "desiccator," whose bottom and sides were well moistened with pure water. The silver was covered with redistilled nitric acid of the usual strength and left covered both by watch-glass and desiccator lid to dissolve slowly over night in a warm place. On the next day the moisture on the glass cover was washed, with great care to avoid the slightest spattering, into the quartz dish. If any spattering occurred it was caught in the large desiccator, which, having been tightly covered, served also to catch all spray proceeding from the solution of the silver. In two experiments, the silver recovered from the water in the desiccator amounted to only 0.02 milligram when estimated by the nephelometer, and in one no silver at all was found in the desiccator.

Hydrochloric acid gas was next allowed to play upon the surface of the silver nitrate solution in the quartz dish, and the resulting chloride was caused to sink to the bottom by means of a very small glass stirrer, afterwards carefully rinsed. The remaining solution of

nitric and hydrochloric acids was then evaporated to dryness upon a clean steam bath under an appropriate hooded cover (Victor Meyer funnel). The atmosphere around was kept as pure as possible during this evaporation, which was usually conducted during the night. Finally the silver chloride was fused in the quartz dish supported inside of a large porcelain crucible from which the products of combustion of the gas-flame were suitably deflected. The weighed cover caught the one or two minute drops projected upward during the act of fusion. Then a mixture of chlorine and hydrochloric acid gas was passed in, so as to convert any residual traces of nitrate of silver wholly into argentic chloride. The precaution of cooling, mentioned on p. 59, enabled us to preserve the quartz dish intact through the analyses, notwithstanding the extreme fragility of thin fused quartz. Its weight was conserved through three experiments within the limits of the accuracy of the weighing. Experiments 83, 84, and 85 were made by this method. One of these is given below in detail as an example of the method.

EXPERIMENT 84.

	Grams.
Corrected weight of silver in air	6.25336
Vacuum correction	0.00018
Weight of silver in vacuum	6.25318
Excess weight quartz dish over counterpoise	0.21510
Excess weight dish and fused AgCl over counterpoise	8.52279
Weight of argentic chloride in air	8.30769
Excess weight cover glass over counterpoise	0.09972
Excess weight cover and spattering over counterpoise	0.09974
Spattering	-0.00002
Weight argentic chloride in air	8.30771
Vacuum correction	0.00061
Weight of argentic chloride in vacuum	8.30832
AgCl found in desiccator by nephelometer	0.00002
Total weight of argentic chloride	8.30834

$$AgCl = 6.25318 : 8.30834 = 100.000 : 132.866$$

This second method, which avoids any transference of material whatever, is an unusually searching check upon the method employing the Gooch filter ; and that the two methods confirm each other to the limit of weighing is a most satisfactory criterion of each, supporting the previous similar work with sodic chloride as well.

The following table is complete, including all the experiments made with the purest material, and every precaution. The experimental work, as well as the preparation work, was the product of more than one experimenter, the senior author having made, from beginning to end, the syntheses numbered R. 2 and R. 3 (as well as R. 1 in the preliminary series),* and the junior author having made all the others. The two experimenters used different balances, different weights separately standardized, and different preparations throughout, in order to secure additional certainty.

For No. 69, Baxter's silver fused on lime in hydrogen was used; for Nos. 77, 78, 80, 81, 83, R. 2, sample T, fused in the same way; for R. 3, sample V, fused on lime in a vacuum, and for 84 and 85 sample W, fused on lime first in hydrogen and then in a vacuum.

Synthesis of argentic chloride.

FINAL SERIES.

Exp.	Observed wt. Ag (vac.).	First approx. weight AgCl (vac.).	Corrections to AgCl.				Corrected weight AgCl in vac.	Parts AgCl produced by 100,000 parts Ag.
			Asbestos residue.	Loss on fusion.	Gain in Cl_2.	Cor. for solubility.		
	Grams.	*Grams.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Grams.*	*Per ct.*
69	7.24427	9.62517	+0.16	—0.40	+0.09	+0.06	9.62508	132.865
77	8.30502	11.03312	+1.10	—0.14	+0.67	+0.09	11.03484	132.870
78	7.29058	9.68547	1.23	0.12	0.09	0.09	9.68676	132.867
80	8.58472	11.40578	0.57	0.32	0.02	0.09	11.40614	132.866
81	8.01318	10.64632	0.34	0.32	0.05	0.09	10.64648	132.862
R. 2	9.77160	12.98283	0.74	0.37	0.02	0.13	12.98335	132.868
83	7.98170	10.60528	.....	.....	.....	.....	10.60528	132.870
Average.	.....	.....	.....	.....	.....	.....	.....	132.867
R. 3	11.49983	15.27978	+0.44	—0.66	+0.03	+0.05	15.27964	132.868
84	6.25318	8.30834	.....	.....	.....	.....	8.30834	132.866
85	7.72479	10.26360	.....	.....	.....	.....	10.26360	132.866
Average.	.....	.....	.....	.....	.....	.....	.....	132.867
Total...	82.66887	.....	.....	.....	.....	.....	109.83951	132.867

This result, namely, 132.867 parts of the chloride from 100,000 of silver, has a "probable error," computed according to the method of least squares of about 0.0005. This so-called probable error of course

*The hydrochloric acid used in these experiments was three times successively treated with small amounts of permanganate and boiled to eliminate bromide, and each time distilled.

gives no clue as to possible constant errors involved. A better idea of the chemical trustworthiness of the result is got by comparing the data furnished by the two different methods of synthesis. The averages of the seven determinations by the method of filtration is 132.8666, while that of the three by the method which involves no transference of material (83, 84, 85) is 132.8673. These are both within the range from the mean 132.8668 indicated by the "probable errors" of the respective averages, and hence may be considered as identical.

If the comparison be made according to the environment of the silver during fusion, a similar result is obtained. The silver fused in hydrogen gives an average of 132.8668, while that fused in a vacuum gives 132.8668. Again this is essential identity.

In view of these facts, the fact that all probable errors tend to lower the result, and the multitude of precautions which eliminated error from these figures, it is not unsafe to conclude that 100.000 parts of the purest silver really yields as much as 132.867 parts of argentic chloride. This conclusion confirms the comparison of the silver and argentic chloride indicated by the work on sodium, and shows that no great occlusion of sodic nitrate could have taken place there. It furnishes, moreover, a means of determining by comparison the purity of any other specimen which has been used in the quantitative synthesis of argentic chloride by either of the foregoing methods. For example, it shows that the silver used in the work on sodium—silver which yielded 132.862* parts of chloride—must have contained $\frac{5}{132867} = \frac{1}{27000} =$ 0.0037 per cent of impurity.

*See Syntheses 65, 66, and 70 given in the table on page 61. The silver used in these syntheses was exactly similar to some of that used in the work on sodium. In the same way, if Stas's method of synthesis is considered as comparable with ours, his silver must have contained (132867 — 132848) ÷ 132867 = 0.015 per cent of impurity. It is doubtful, however, if the methods of synthesis are strictly comparable.

THE NEW ATOMIC WEIGHTS OF SODIUM AND CHLORINE AND THEIR EFFECT ON OTHER ATOMIC WEIGHTS.

From the preceding description of the syntheses of argentic chloride, it is clear that 100.000 grams of the purest metal yields 132.867 grams of chloride. If then the atomic weight of silver is taken as 107.920* (a convenient value to assume for preliminary calculation), the molecular weight of argentic chloride becomes by simple proportion 143.393, and by difference the atomic weight of chlorine becomes 35.470.† This value is about 0.05 per cent greater than the value announced by Stas ; and the change produces a serious effect on a number of atomic weights. It is, of course, impossible to be perfectly certain of the accuracy of the new value, because it may contain concealed within it some entirely unsuspected source of error, but at least it is free from the real mistakes in the earlier work. It was reasonably certain that at least ten more syntheses would be needed to affect the value one unit in the third decimal place, if the further results varied no more widely than those recorded above in the final series. Hence it seems unlikely that chlorine is above 35.471 or below 35.469 if silver is taken as 107.920.

What, now, is the effect of this new value upon the atomic weight of sodium? In the table given upon page 44 it is shown that 100.000 grams of argentic chloride could be obtained from 40.780 grams of sodic chloride. If now argentic chloride is taken as 143.390, sodic chloride becomes 58.474, and by subtracting the new value for chlorine, 23.004 is obtained as the new value for sodium.

This is not, however, the only value for sodium which may be calculated from our results. On page 52 has been given a table showing the results of ten experiments on the comparison of sodic chloride with silver direct, and on page 56 the results of two more. These determinations were made before we had discovered the best method of obtaining pure silver ; but the trace of impurity is allowed for in those tables, and it is safe to conclude that 100.000 parts of the purest silver are equivalent to 54.185 parts of sodic chloride. If, then, silver is taken as 107.920 and chlorine as 35.470, sodium becomes 23.007.

Thus two entirely independent values, calculated from two entirely separate series of experiments, yield respectively the values 23.004 and 23.007 for the atomic weight of sodium. Of these two, the latter is

*F. W. Clarke has for a long time accepted this value, and it is now assumed because it is probably nearer the true value than 107.93.

†In this connection it should be pointed out that Leduc called attention to the fact that if Stas's silver really contained as much oxygen as Dumas said it must, chlorine would become 35.47. Compt. Rend. (1901).

somewhat the more trustworthy, because, as has been said, the occlusion of sodic nitrate by the precipitate does not affect it; hence the mean may be taken as 23.006. This value is probably not more in error than two units in the third decimal place, if silver is 107.920, although of course the same remark applies to it that was made concerning the possible error of the value for chlorine. If silver is taken as 107.930, sodium becomes 23.008, and chlorine 35.473. The new values are, then, as follows:

	(Ag=107.920).	(Ag=107.930).
Atomic weight of sodium.....	23.006	23.008
Atomic weight of chlorine	35.470	35.473

The new value for sodium is nearly 0.2 per cent less than that found by Stas—a percentage error much greater even than that made by him in the case of iodine. It will be noted that the likely error of the new result is only about a twentieth of the difference between the new result and that of Stas. Some will attach significance to the fact that both the new values bring the elements nearer to the demands of Prout's hypothesis.

These new values affect greatly the figures in the second decimal place of all other atomic weights depending directly or indirectly upon chlorine, sodium, or silver. The number of elements thus affected is so great and the relations so complicated as to render imperative a recalculation of all atomic weights. Nitrogen, as computed from ammonic chloride, will be especially affected, the new value approaching more nearly that required by Avogadro's rule than the old. Probably, however, it will be best to delay this systematic recalculation until a few other new data shall have been obtained—in particular new analyses of potassic chloride, argentic chlorate, the bromides, sulphides and sulphates, and similar important compounds. Some of these are already under way at Harvard, and others will be undertaken at once.

In conclusion, it is a pleasure to acknowledge our great indebtedness to the Carnegie Institution of Washington, without whose liberal support the present investigation could not have attained its present thoroughness or precision.

SUMMARY.

The investigation consisted of a very careful quantitative study of three ratios—namely, AgCl : NaCl, Ag : NaCl, and Ag : AgCl. The effort was made to test every operation involved in the execution of the experiments. In the course of the work, the following points were developed:

1. Sodic chloride, obtained from many sources and purified in many ways, always gave the same equivalent weight.

2. Fusion in vacuum of salt already fused in air caused no change in this equivalent weight.

3. Argentic chloride precipitated from aqueous solutions always occludes traces of other substances present, and those traces can not always be eliminated. Very dilute solutions must hence be used in precipitation.

4. The conditions governing the occlusion and release of these impurities were minutely studied, and it was shown that Stas's method of dropping solid salt into a silver solution causes occlusion of salt. Many considerations important in all precise chemical work are discussed.

5. A careful study of the solubility of argentic chloride was made, and the precautions necessary in using the nephelometer in the estimation of traces of chloride and silver were ascertained.

6. Fused argentic chloride probably contains traces of dissolved air, but not enough to affect essentially its weight, since subsequent fusion in vacuum caused no appreciable loss of weight.

7. The most difficult question in the purification of silver was found to be the elimination of the inclosed mother liquor without introducing other impurities. Fusion on pure lime, first in pure hydrogen and then in a vacuum, is the safest method. Stas's silver must have contained at least as much oxygen as Dumas claimed.

8. In ten experiments, 44.5274 grams of sodic chloride yielded 109.1897 grams of argentic chloride.

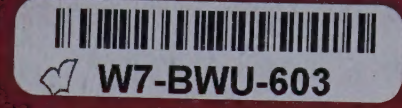
9. In twelve other experiments, entirely distinct from these, 49.5007 grams of sodic chloride were found to be equivalent to 91.3543 grams of the purest silver.

10. In ten other experiments, again entirely distinct from the preceding, 82.6689 grams of the purest silver yielded 109.8395 grams of argentic chloride. Two very different methods of synthesis were used in this series, and the silver came from various sources, these variations being without effect on the result.

11. If the atomic weight of silver is assumed to be 107.920, sodium is found from the above results to have an atomic weight of 23.006 and chlorine an atomic weight of 35.470.

12. Many other atomic weights are affected, in their second decimal places, by these changes. In particular, certain slight anomalies previously noticed in Harvard work are explained by them, and the atomic weight of nitrogen computed from ammonia is brought nearer to the value required by Avogadro's rule. Other anomalies appear in other places, however, and it is clear that many new atomic-weight investigations must be instituted to explain them, with due attention to hitherto unheeded dangers, especially of occlusion.

Withdrawn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